

A NEW PERSPECTIVE ON THE NATURE OF "ORGANIC" SULFUR IN COAL.

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INTRODUCTION

It is generally assumed that the sulfur in coal is distributed among organic sulfur, sulfatic sulfur, and pyritic sulfur compounds (1). ASTM D-2492 which lists the forms of sulfur in coal also assumes that three forms are present--sulfatic, pyritic, and organic sulfur. The organic sulfur value of coal is derived as the difference between the total sulfur content of coal and the amount of pyritic plus sulfatic sulfur i.e., any form of sulfur that is not pyritic or sulfatic sulfur would be counted as organic sulfur. The organic sulfur is generally perceived to occur in covalently bonded C-S compounds like thiophenes, thioethers, and bithioethers (disulfides) (2,3). Elemental Sulfur, which would be accounted for as "organic sulfur", has been mentioned, only in a few references in the literature. Yurovskii (4) in his monumental treatise on 'Sulfur in Coals' provides evidence for the presence of elemental sulfur in coals. Richard, Vick and Junk (5) and White and Lee (6) confirmed the presence of elemental sulfur for several bituminous American coals. In a more recent article, Lee et al (7) report the detection, in a Bevier seam coal, of 3,6-dimethylbenzo(b)thiophene that can be potentially formed by reaction of elemental sulfur with terpenes (Figure 1). Further light on this question was provided by De Roo and Horton (8,9) when they demonstrated that elemental sulfur reacts with simple alkyl aromatics, under mild conditions, to give thiophenic compounds. De Roo (8) showed that such reactions can occur under geochemical settings and conclude that the generation of organic S compounds in petroleum followed this route. Thus, the reaction of elemental sulfur with coal aromatics could, in part, account for the formation of organosulfur compounds found in coal (Figure 2). However, Stock et al.(10) report that pristine coal samples (from the Argonne Premium Sample Coal Bank) are free of elemental sulfur. He suggests that sulfur is not a natural constituent of coal, but that on exposure to air, elemental sulfur, which can account for up to 5% of the total amount of sulfur in the sample, is formed.

In this paper we present a new perspective on the nature of organic sulfur in coal and suggest that the organic sulfur fraction in pristine coal contains sulfur in the form of a coal-polysulfide complex (see Figure 3-- an elemental sulfur precursor) which, in some coals, may constitute in excess of 50% of the organic sulfur fraction. Under suitable chemical/biological environments, this sulfur complex would give rise to free elemental sulfur. The sulfur, thus set free could get dispersed through the coal matrix and would be present in the amorphous form. The amorphous form arises when sulfur precipitates from solution as a result of chemical-reactions, especially when it first appears in the colloidal state. This sulfur would be insoluble in organic solvents and would not be detected by X-ray diffraction.

Experimental evidence using solvent extraction studies (under conditions that will allow the extraction of amorphous sulfur form) and geochemical approaches is presented below supporting the concept of this new polysulfide sulfur form in the "organic" sulfur fraction of coal. If this is true, then research and development efforts to remove the so-called organic sulfur components in coal must take into account this factor., especially since the elemental sulfur or the polysulfide sulfur can react with alkyl aromatic structures in coal creating new thiophenic sulfur compounds from which it is very difficult to excise the sulfur.

EXPERIMENTAL

An Illinois No.6 coal (Herrin No. 6 coal from a west central Illinois Underground mine) from the Illinois Basin Coal Sample program (IBCSP, sample No. 1), the corresponding pristine Illinois No. 6 coal from the Argonne Premium Sample Coal Bank and an Indiana bog(reject) coal were selected for extraction studies. Table 1 shows the sulfur analysis for the three coals studied.

TABLE 1
Analysis for Forms of Sulfur in Coals Studied

Coal	Organic %	Pyritic %	Sulfatic %	Total %
IBCSP No.1	3.00	1.20	0.06	4.26
Pristine Coal				
Indiana Bog	3.33	5.20	4.48	13.01

2g of the coal (accurately weighed) were extracted with perchloroethylene solvent at different temperatures and the extract concentrated. The concentrate was diluted to mark in a 25ml volumetric flask and the amount of sulfur determined using GC-MS. The sulfur quantization was carried out using a Finnigan 4000 gas chromatograph/mass spectrometer (San Jose, CA). A 6' x 2 mm i.d. SP2100 on 80/100 Supelcoport chromatographic column was used with a helium flow rate of 35 ml/min. For these analyses, both the column and injector temperatures were held constant at 180°C. The ion source temperature of the mass spectrometer was set at 180°C. The electron energy was set at 70eV and the electron multiplier 1600eV for these analyses. The mass analysis was carried out using multiple ion detection (MID).

In order to quantitate, a standard curve was first obtained using the following series of standards; 0.005% , 0.01% , 0.025% , 0.05% , 0.1% , and 0.5% sulfur. Five microliters of both the standards and samples were injected on-column. The criteria for confirmation of sulfur was two-fold: 1) retention time and 2) relative ratio of the three sulfur ions used in the MID program (m/z 64:192:256; 10:2:1). The standards were run again after the samples to determine the stability/reproducibility of the ion intensities within the mass spectrometer over the total time of the analysis. The peak area of the m/z 64 ion was used in the quantitation.

RESULTS

COAL SAMPLE STUDIES

Perchloroethylene extraction of Illinois Coal

Perchloroethylene is an excellent solvent for solubilizing elemental sulfur. The solubility is ~ 30g S/ 100g Solution as opposed to only 0.066g S/ 100g Solution in Ethyl Alcohol or 2.7g S/ 100g Solution in Acetone. The Illinois Basin Sample Coal Program sample No.1 (-100 mesh) (IBSCP sample 1) was extracted with perchloroethylene at 120°C and the results of three different runs gave an average elemental sulfur content of 1.54% for the coal sample Table 2).

TABLE 2
Elemental Sulfur in Illinois Coals

Coal/Run No.	% Elemental S	Average %	Elemental S as % of Organic S	Elemental S as % of Total S
IBCSP-1	1.50			
IBCSP-2	1.62	1.54	51.3	36.1
IBCSP-3	1.50			

This means that 51.3% of the so called "organic" sulfur or 36.1% of the total sulfur is present as elemental sulfur. Stock et. al. (10) report that only 2% of the total sulfur in the same type of coal (IBSCP sample 1) was elemental sulfur. However extraction of a pristine Illinois No.6 coal from the Argonne

Sample Coal Bank gave no elemental sulfur within the detection limits used. An Indiana Bog (Reject) coal was extracted with perchloroethylene at different temperatures and as shown in Table 3 there was a 59% increase in the amount of elemental sulfur extracted in going from room temperature to 120°C. The 1.23% elemental sulfur extracted at 120°C amounts to 36.9% of the "organic sulfur" in that coal.

TABLE 3
Effect of Temperature on Sulfur Extraction

<u>Temperature</u>	<u>% Elemental S extracted</u>
Room Temp.	0.78
60°C	1.08
120°C	1.23

Geochemical Approaches

Fresh coal samples from the Minnehaha Mine, Sullivan County, Indiana was used in the study. The method of sampling which was described by Parratt and Kullerud (11) assures that unoxidized specimens are obtained. The samples were divided into approximately equal amounts and placed in ten double polyethylene plastic bags which were sealed airtight and directly transported to storage containers in the Purdue laboratories. One bag was opened within hours upon arrival at the laboratory and its content was exposed its warm, humid air. Oxidation products in the form of a yellowish-brown or other colored powder started to form within days, was quite distinct after one week, and occurred in significant amounts after one month. X-Ray powder diffraction charts made on this substance displayed the characteristic reflections of iron-calcium-aluminum sulfates. The color and texture of this substance are similar to those of elemental sulfur. However, the X-ray powder diffraction reflections of sulfur were not observed. The sulfur, if present, may be amorphous.

A number of polished sections were made on material from a second bag and under the reflected light microscope it was noted that pyrite, marcasite and sphalerite make up about 2% of this coal. Pyrite is most common, marcasite much less so and only one or two grains of sphalerite were observed in each section. Sulfates of any form or elementary sulfur were never observed in freshly made polished sections. Four stages of iron sulfide mineralization are distinguishable; framboidal pyrite, marcasite, fibrous pyrite and massive pyrite. Although these sulfides generally are evenly distributed throughout the coal it was possible to localize areas which contained no visible sulfides. Accordingly, fresh samples from a third bag were gently crushed to about 2 mm size and placed in badges of a few grams at a time under the zoom lense of a binocular microscope. It was now possible to quite efficiently separate grains of coal with no visible sulfides. Several grains of this material were next exposed to warm, humid air. Oxidation products again became visible in a few days. The products were the same, but their amounts were much smaller than those which previously were produced under identical conditions in equal time from the original unseparated coal. About one dozen of the coal grains, containing no visible coal, were mounted in low temperature curing epoxy and polished. Less than 0.05% iron sulfide was observed in the polished surfaces under the reflected light microscope. In such grains sporinite is the most common maceral. Vitrinite, cutinite, and resinite are much less common, and fusinite, sclerotinite are the least common. Microprobe analyses were performed on selected sulfide-free areas of polished surfaces of numerous grains. Analyses revealed that sporinite has a sulfur content of about 2.9 to 3.0%, whereas vitrinite, cutinite and resinite contain from 1.1 to 1.4% S and fusinite, sclerotinite contain about 0.25% S (12).

Simultaneous analysis on iron and sulfur in areas where sulfides are not detected in polished sections always gave Fe values of less than 0.1% Fe. The sulfur concentrations cited above reflect the values remaining upon subtraction of the sulfur required to convert all Fe to FeS₂; in other words, it was assumed that all detected iron is present as disulfide. Thus it becomes apparent, that at least in this particular coal, the concentration of the sulfur which we usually refer to as organic is strongly dependent on the type of maceral in which it occurs. Sulfur is, for instance, almost three times as abundant in sporinite as it is in vitrinite which in turn contains four times as much sulfur as do the typical inertinite macerals.

It is also quite apparent that a significant portion of this maceral sulfur reacts with warm and humid air to produce sulfates and amorphous elemental sulfur. In a series of experiments conducted on the

material contained in a fourth sample bag, total sulfur was, by wet chemical analysis on a representative 5 gr sample, found to be 3.2 ± 0.2 wt%. The sulfide sulfur determined by separating physically and weighing the sulfides from a representative 1 gr sample gave 1.8% sulfide sulfur after correcting, through polished section study, for remaining unseparated sulfides. Wet chemical analysis of the remaining "pure" macerals, which contain less than 0.05% wt Fe and less than 0.2% Al accounted for as clay minerals, gave 1.2 ± 0.2 wt%. Treatment of these "pure" macerals, which had been crushed as cited above, with warm, humid air produced the ocher colored material. This was carefully removed from the maceral grains. New analysis on a portion of the cleaned maceral grains indicated a sulfur concentration of 0.9 wt%. The remaining portion of the cleaned maceral material was finally treated with distilled water for several days at 60°C on a waterbath. Careful processing involving decanting prior to washing in distilled water, repeated decanting and slow drying at 110°C was followed by a final sulfur analysis. This gave 0.6 wt% S. This would indicate that about 50% of the so-called "organic" sulfur can be removed by exposure of the macerals to hot, humid air and to pure warm water. Conservatively stated: at least a portion of the so-called organic sulfur in coal macerals occurs under chemical conditions which permit it to react with oxygen in the air and with water. The character of the chemical bonds involving this particular sulfur is not known, but at least the generally perceived carbon-sulfur bonds are precluded.

DISCUSSION

Both chemical solvent extraction and geochemical studies strongly indicate that the so called "organic" sulfur fraction of coal contains a major sulfur form different from the conventional thiophenic and thioether type structures normally associated with the "organic" sulfur fraction. A coal - polysulfide complex as shown in Figure 3 is suggested. Under suitable chemical/geochemical conditions, this sulfur complex would give rise to free elemental sulfur. This would account for the fact that no elemental sulfur is detected in the Argonne pristine coal sample, however the not so pristine samples from the IBCSP would undergo reaction to yield elemental sulfur. The sulfur, thus set free could get dispersed through the coal matrix and would be present in the amorphous form. Crystalline sulfur (orthorhombic and monoclinic) consist of ring shaped molecules containing eight atoms (Figure 4) and is soluble in common organic solvents like CS₂ and acetone. Amorphous sulfur, on the other hand, results when the ring molecules of sulfur break and successive atoms link together to form a long chain molecule (Figure 4). This would be insoluble in organic solvents and not detected by X-ray diffraction studies. Amorphous sulfur is not stable at temperatures below 160°C and reverts to the crystalline ring-molecule form. This change, however, is extremely slow at room temperatures and at room temperature, amorphous sulfur remains for years with little change (13). At temperatures near 100°C the change from amorphous to crystalline sulfur is more rapid, and practically all amorphous sulfur disappears at this temperature in the course of an hour. The amorphous form arises when sulfur precipitates from solution as a result of a chemical reactions, especially when it first separates as a colloidal dispersed system.. This fits in nicely with the 59 % percent increase in elemental sulfur obtained on going from room temperature to 120°C. It may also be the reason why other investigators using x-ray or solvent extractions at or near room temperatures have not observed appreciable amounts of elemental sulfur. The behavior of the amorphous sulfur is further illustrated in the well known **vulcanization of rubber** using sulfur. In this, a part of the sulfur used for vulcanization remains unreacted, and the vulcanized rubber always contains a certain amount of free sulfur. In the hot vulcanization process, the free elemental sulfur is in crystalline and can be readily extracted with hot acetone or carbon tetrachloride. However, if the vulcanization is effected in the cold, the free sulfur is formed in the metastable amorphous modification and is finely dispersed. It is not extractable even, with good sulfur solvents like CS₂.

The fact that the coal - polysulfide complex can, under appropriate conditions spit out elemental sulfur is supported by observations on model compounds. Thus, Diethyl Xanthogen trisulfide on treatment with moist acetone forms the disulfide and elemental sulfur while, Diethyl Xanthogen tetrasulfide also yields the disulfide and eliminates two sulfur molecules (14) (Figure 5). One fact that needs to be stressed is that a portion of the sulfur contained in higher polysulfides is so loosely bound that they behave as elemental sulfur and thus, in many reactions behave like elemental sulfur.

IMPLICATIONS

The existence of coal-polysulfide complexes that may yield elemental sulfur and take part in elemental sulfur reactions brings up an important new factor in R&D approaches to removing "organic"

sulfur in coal and for coal processing in general. As shown by White and others (6-9) elemental sulfur can react with alkyl aromatics to form thiophene compounds (Figure 2). Our concern is that coal processing operations result in creation of hard to remove covalent C-S bonded structures like the thiophenes from the more easily removable polysulfide type structures. Even more damaging is the fact that thiophenic crosslinks between coal clusters could arise resulting in the creation of a even more intractable macromolecule (Figure 6) that would be more difficult to process.

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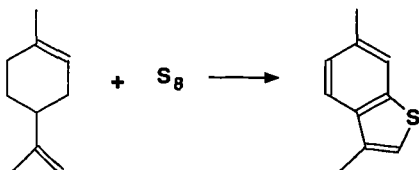


Figure 1. Formation of Thiophenes with Elemental Sulfur. From Ref. 7

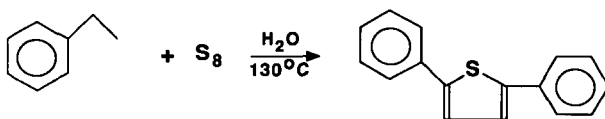
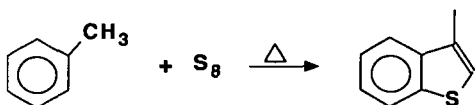


Figure 2. Reaction of Elemental Sulfur with Alkyl Aromatics. Formation of Organosulfur Compounds

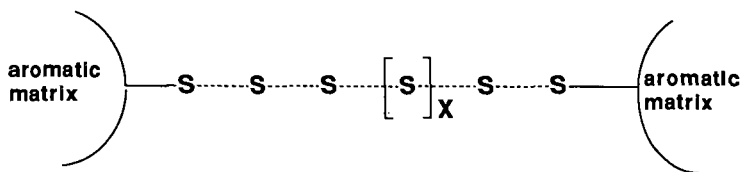
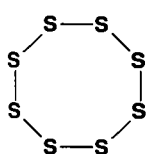
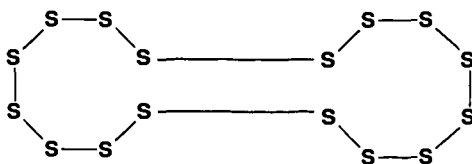


Figure 3. Conceptual Coal-Polysulfide Complex



Crystalline Sulfur



Amorphous Sulfur

Figure 4. Structure of Crystalline and Amorphous Sulfur

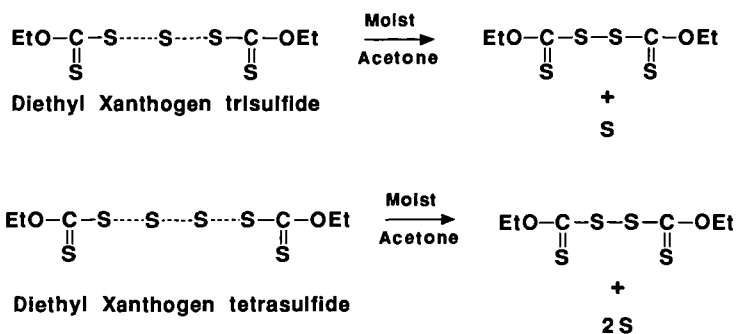


Figure 5. Model Organo-polysulfide Complex Spitting out Elemental Sulfur under Appropriate Conditions

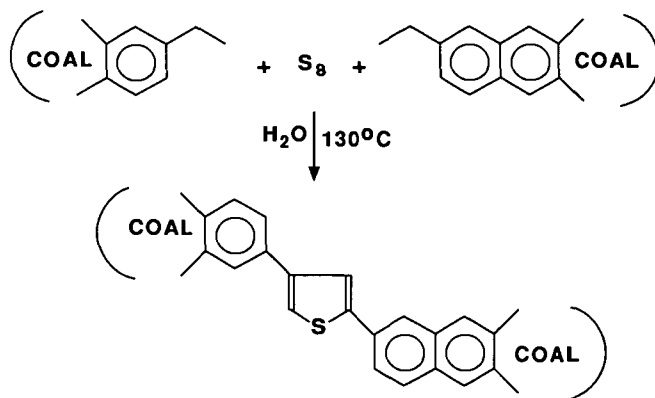


Figure 6. "Crosslinking" of Aromatic Coal Clusters via Thiophenic Bridges

EXAFS INVESTIGATION OF ORGANIC SULFUR IN COAL

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ABSTRACT

EXAFS spectroscopy is shown to be a very promising technique for investigating the molecular structure of organically bound sulfur in coal and coal derivatives. The current paper presents sulfur K-shell EXAFS results for a number of maceral separates prepared by density gradient centrifugation and for several biodesulfurized coals. Both the near-edge structure and the radial structure functions exhibit some similarities to dibenzothiophene. However, a broad peak occurs in the XANES region of the coal spectra that is not observed for the molecular structures usually ascribed to organic sulfur in coal. This is believed to arise from resonant photoelectron scattering from second and third nearest neighbor carbon shells and from sulfur bonded to oxygen.

Introduction

Numerous techniques are available for investigating the structure of the inorganic forms of sulfur in coal and coal derivatives. These include ^{57}Fe Mössbauer spectroscopy,^(1,2) computer-controlled scanning electron microscopy,^(3,4) and x-ray diffraction,^(5,6) to mention a few. The development of techniques to determine the structural forms of organic sulfur, however, has proven more difficult. Recently, it has been demonstrated that X-ray absorption fine structure spectroscopy, usually referred to as EXAFS spectroscopy, is a very promising method for investigating the molecular structure of organic sulfur in coal.^(7,8) In this article, some recent EXAFS results obtained from maceral separates and other samples containing little or no pyrite are summarized.

Experimental Procedures

EXAFS spectroscopy provides information on the electronic bonding and atomic environment of an element through detailed analysis of the fine structure associated with an X-ray absorption edge of that element. When a synchrotron radiation source is used, individual elements can be investigated at dilute levels (~ 100 ppm to 1%) in complex samples. The current experiments were conducted during a dedicated run at the Stanford Synchrotron Radiation Laboratory using wiggler beam-line VII-3. Electron energies were 3 GeV and beam currents were typically 40 to 80 mA. A Si(111) double crystal monochromator was used to vary the X-ray energy from approximately 100 eV below to 600 eV above the sulfur K-shell absorption edge (2472 eV). To minimize absorption of these relatively soft X-rays, an all helium pathway from the beam pipe to the sample and detector was constructed and thin (6 μ m) mylar windows were used wherever possible. The experiments were done in the fluorescent mode, using a fluorescent ionization detector described elsewhere.⁽⁹⁾

Most of the samples examined were maceral separates prepared by density gradient centrifugation (DGC). Discussions of the DGC methods are given elsewhere.⁽¹⁰⁻¹²⁾ EXAFS measurements were made on exinite, vitrinite and inertinite separates from coals of several ranks. In addition to maceral separates, several coals from which all pyrite had been removed by biological desulfurization⁽¹²⁾ were examined. The EXAFS specimens were prepared in the form of pellets by hydrostatically pressing the coal powder into a boric acid cylinder or, in some cases, adding an epoxy binder.

Results and Discussion

EXAFS spectroscopy determines the electronic structure and atomic environment of an element by analysis of the fine structure associated with an X-ray absorption edge of that element. The spectra are normally divided into two regions. The region within about 20 to 50 eV of the absorption edge is called the X-ray absorption near edge structure, or XANES (see Figures 1 and 2). The peaks and other structure in this region are derived primarily from two sources: photoelectron transitions to vacant, bound levels,^(13,14) and low-energy scattering resonances.⁽¹⁵⁻¹⁷⁾ The XANES spectra are quite sensitive to the detailed nature of the electronic bonding and can frequently serve as fingerprints to identify different compounds or types of binding.

The extended X-ray absorption fine structure, or EXAFS, is the oscillatory structure that begins at 30 to 50 eV above the edge and extends to fairly high energies (~ 500 to 1000 eV). These oscillations arise from interference between the outgoing and backscattered photoelectron wave functions. They can be subjected to a Fourier transform analysis to yield a radial structure function (Figure 3) from which interatomic distances and coordination numbers for the atomic neighbor shells of the absorbing atoms can be determined.^(18,19)

Typical sulfur K-shell EXAFS data are shown in Figures 1 to 3. The XANES of several standard compounds appear in Figure 1. The zero of energy is taken at the first peak in the differential of the spectrum of elemental

sulfur. The first large peak in the XANES, the so-called "white line", probably arises from a transition of the photoelectron from the 1s level to hybridized p levels - 3p/3d-4s for pyrite and 3p/2p for the remaining compounds. The subsequent broader peaks, located between approximately 5 and 30 eV for pyrite and dibenzothiophene (dbt), and from 15 to 40 eV for the sulfur-oxygen bonded compounds, probably arises from low energy scattering resonances.(15-17) It is evident that the increase in valence of the sulfur ions bonded to oxygen in sulfosalicylic acid and ferrous sulfate causes a significant positive shift in the white line and other XANES features.

XANES spectra of several maceral separates from a high volatile bituminous coal (PSOC 733, HVAB, Appale, PA) are shown in Figure 2. The first two peaks, which are relatively sharp, occur at the same locations and have similar intensities to the corresponding peaks in the XANES of dbt. Presumably, they represent s \rightarrow p transitions characteristic of an aromatically bound sulfur atom. Thianthrene, however, which contains two aromatically bound sulfurs, exhibits only the first of these two sharp peaks, at approximately 3 eV. This could reflect the increase in symmetry of the sulfur sites in thianthrene.

The broad peak at 10-11 eV was observed for all coal specimens examined, but was not present in the XANES of any standard compounds in which S is bonded to C and H. It is in approximately the same location as the strong white line in the XANES of the standard compounds that contain S bonded to O (sulfosalicylic acid and various sulfates). Consequently, sulfur oxidation may be partially responsible for this feature. However, it is seen in Figure 1 and Table I than sulfur-oxygen bonded species also exhibit significant secondary XANES structure between 20 and 30 eV that is not evident in the coal spectra. It seems likely, therefore, that low energy resonant scattering of the photoelectron by second and third neighbor shells may be the primary origin of the broad peak at 10-11 eV. As discussed elsewhere,(15-17) the position of such scattering peaks can be related to interatomic distance. It has previously been noted^(16,17) that an $ER^2 = \text{constant}$ relation frequently holds for such XANES features, where E is the energy at which the peak occurs and R is the distance from the absorbing atom to the neighbor shell which gives rise to the scattering resonance. Dependent on what reference point the peak energy is measured from, the effect of phase shifts on the E - R relation, and multiple versus single scattering, distances of approximately 2.5 to 4 Å could be compatible with the peak in question. Work is now in progress to establish suitable energy vs. distance calibration curves from analyses of the XANES of various standard sulfur compounds.

Typical radial structure functions (RSF's) produced by Fourier transformation of the EXAFS of maceral separates are shown in Figure 3. It appears that two atomic shells, and possibly three, can be resolved. Assuming that the atoms surrounding the sulfur in coal are primarily carbons, the standard back transform analysis of the RSF peaks was carried out using an empirical S - C phase shift determined from the EXAFS data for dbt. The interatomic distances determined in this manner seem reasonable (Table II).

Conclusions

The current results demonstrate that EXAFS spectroscopy is an excellent method for direct, non-destructive, investigation of the molecular structure of organic sulfur in coal. Future studies will concentrate on development of calibration relationships for interpretation of the XANES, and conducting in situ studies of the changes in sulfur structure resulting from pyrolysis, hydrogenation, and oxidation.

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TABLE I. Energies (eV) of the first three peaks observed in the XANES of some standard compounds and coal specimens. Peak 1 is the most intense XANES feature.

Sample	Peak 1		Peak 2		Peak 3	
	Position (eV)	Area ⁺ (%)	Position (eV)	Area (%)	Position (eV)	Area (%)
K ₂ SO ₄	11.5	62	15.1	6	17.3	32
thianthrene	3.3	66	9.4	34		
4,4 thiodiphenol	2.5	26	4.1	15	10.7	52
sulfamic acid	9.0	41	11.5	31	18.0	27
sulfosalicylic acid	10.3	83	16.9	17		
dibenzothiophene	2.8	60	4.8	9	8.3	31
2,2 thiodiacetamide	2.6	17	7.8	27	18.5	56
thioacetamide	0.1	42	2.4	13	5.8	46
pyrite	0.9	94	8.9	3	11.8	3
pyrrhotite	-0.5	7	6.8	32	12.0	54
W. KY #9, run 6, biodesul.	2.9	37	5.0	6	11.4	57
W. KY #9, run 5, biodesul.	2.9	32	4.9	4	11.7	64
PSOC 733 (e)	2.8	47	4.9	7	11.3	46
PSOC 733 (v)	2.9	43	4.7	6	11.3	51
PSOC 733 (i)	2.9	41	4.9	3	11.6	56
PSOC 1111 (e)	3.3	41	5.1	23	10.2	36
PSOC 1111 (v)	3.3	39	5.0	24	10.0	37
PSOC 1111 (i)	3.3	43	5.0	24	9.9	33
PSOC 1110 (e)	3.0	46	4.8	20	9.8	34
PSOC 1110 (v)	2.4	26	4.1	9	9.1	73
PSOC 1108S (v)	2.5	21	4.2	9	9.4	78
W. KY #9 (e)	2.9	41	4.8	4	10.8	55
W. KY #9 (v)	2.9	40	5.0	5	10.8	55
W. KY #9 (i)	2.9	35	4.9	1	11.2	64
W. KY #9 (v)	2.9	44	4.9	10	11.2	46
W. KY #9 71095 (v)	2.9	48	4.9	6	11.2	46
W. KY #3 (v)	2.2	38	4.2	5	9.9	57
W. KY #5 (v)	2.2	38	4.1	5	10.3	57
W. KY #6 (i)	2.1	45	4.0	5	10.7	50

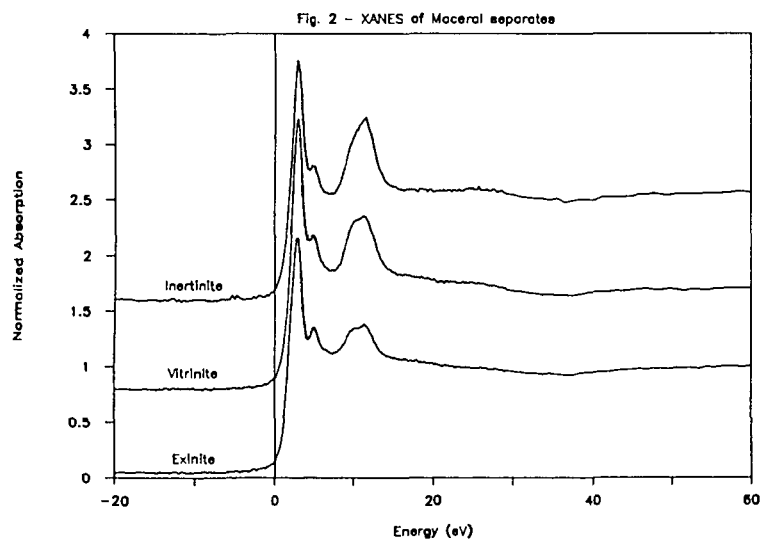
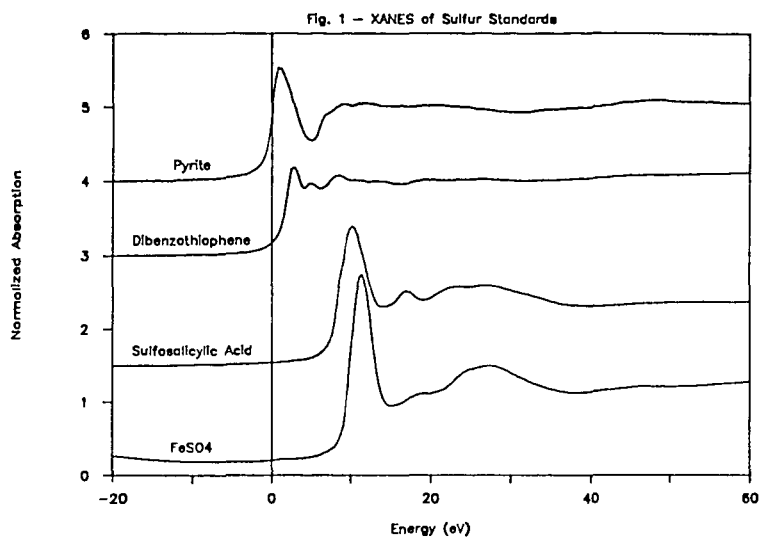
*(e), (v), and (i) denote exinite, vitrinite, and inertinite separates prepared by DGC.

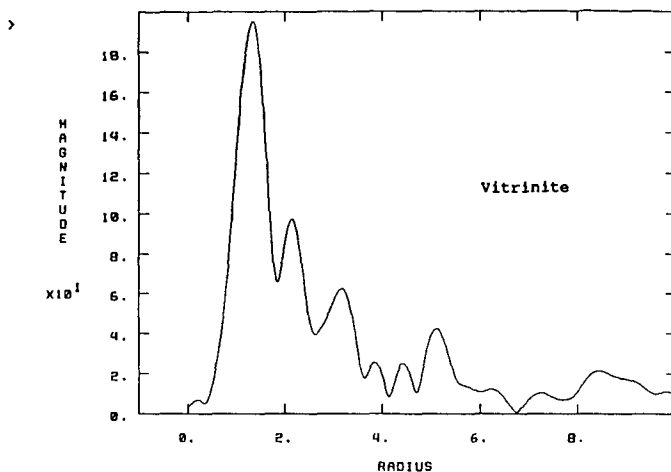
⁺The area percentages are determined by a program developed by one of the authors (R. B. Gregor) that fits the XANES peaks with Lorentzians and the edge step by an arctangent function. The analyses were carried out from -10 to +20 eV.

TABLE II. Distances (Å) from the sulfur atom to its nearest neighbor shells in dibenzothiophene and a variety of coal specimens.

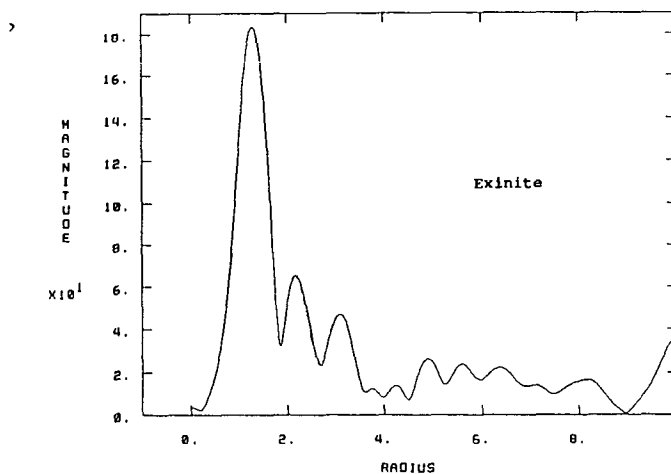
Sample*	Shell 1	Shell 2	Shell 3
dibenzothiophene	1.74	2.71	4.02
W. KY #9, run 6, biodesul.	1.75	2.75	
PSOC 733 (e)	1.75	2.75	4.02
PSOC 733 (v)	1.74	2.74	4.02
PSOC 1111 (e)	1.74	2.74	4.02
PSOC 733 (i)	1.74	2.73	
PSOC 1111 (e)	1.74	2.75	4.05
PSOC 1111 (i)	1.74	2.73	4.02
PSOC 1110 (e)	1.74	2.76	
PSOC 1110 (v)	1.74	2.75	
PSOC 1108S (v)	1.74	2.75	
W. KY #9 (e)	1.78	2.74	
W. KY #9 (v)	1.75	2.74	
W. KY #9 (i)	1.75	2.82	
W. KY #9 (v)	1.75	2.73	
W. KY #9 71095	1.75	2.75	
W. KY #3 (v)	1.75		
W. KY #5 (v)	1.75	2.77	
W. KY #6 (i)	1.74	2.80	

*(e), (v), and (i) denote exinite, vitrinite, and inertinite separates prepared by DGC.





SHACAD.303 3/1 11-JAN-88



SHACAD.300 3/1 11-JAN-88

Figure 3. Radial structure functions obtained from the EXAFS of maceral separates from PSOC 733.

DESULFURIZATION OF PURE COAL MACERALS

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The objectives of this study were to modify the present density gradient centrifugation (DGC) techniques for coal macerals (1-6) to obtain 10-20 grams of target maceral concentrates and to determine the reactivity or ease of removing the organic sulfur in the various macerals with supercritical methanol extraction. Although the chemistry needed for this objective is not difficult, the accumulation of 10 to 20 gram quantities of "pure" petrographically verified single maceral concentrates has not been possible until now. The results of recent work (7) have demonstrated that the individual macerals can be separated and verified. The accumulation of much larger quantities than have previously been separated was a problem that has been overcome by pre-concentrating target macerals at their density cut points.

Supercritical fluid extraction of coals has previously been reported as a method in the production of liquid fuel products from coal under mild conditions and as a medium for selective desulfurization of coal (8-11). Alcohols are expected to exhibit greater solubility for polar organic molecules due to hydrogen bonding and dipole attractive forces, also providing the opportunity for chemical reactions during the extraction due to the nucleophilicity of the alcohol oxygen and the tendency to act as a hydrogen donor. In addition, enol rearrangements (12) may play a role in desulfurization.

As previously reported (8-9), different supercritical reaction conditions produced different extents of desulfurization of coals (33.9 - 65.7%). These variable desulfurizations are probably a result of differences in extents of conversion of the pyritic sulfur (to various alteration products, such as pyrrhotite), as well as organic sulfur functionalities (thiophenol, sulfide, and thiophenes) to light gases such as dimethylsulfide, hydrogen sulfide, and methylmercaptans.

EXPERIMENTAL

Maceral Separation

In this research, the DGC technique was modified and improved to obtain larger size samples. This was done in two ways. First, the coal was divided into its natural divisions, lithotypes, which are the easily identifiable natural associations of macerals that make up the coal seam. This can be done (and routinely is being done in the SIU-C Maceral Separation Laboratory) by careful hand-picking, or by centrifugation at a particle size (-100 to -200 mesh) that liberates the lithotypes

from each other. Even such similar macerals as pseudovitrinite and normal vitrinite are being successfully separated from each other now in this manner. Second, low frequency maceral phases (those occurring at less than 5% of the whole coal) can be pre-concentrated by centrifugation of bulk quantities (10 grams or more) at the density cut-off points for the target macerals. This procedure results in fractions which are enriched in the target maceral relative to the whole coal and allows relatively larger amounts of pure macerals to be obtained much more easily than starting with the raw coal. These pre-concentrated feedstocks are then subjected to the DGC technique.

Target macerals for this study include sporinite, vitrinite, pseudovitrinite, semifusinite and fusinite. These are the major maceral components which contain significant organic sulfur. Resinite and cutinite were not studied because the abundance of these macerals is low in Illinois coals and they contain relatively low concentrations of organic sulfur.

Desulfurization

The desulfurization of coal by supercritical methanol extraction was carried out in a microautoclave system (11) that consists of a 10cc stainless steel microautoclave linked to a metering valve and a quick disconnect fitting with high pressure tubing. The reactor system is attached to an automatic shaker, which is supported above a fluidized sand bath. The shaker allows the autoclave to be agitated during reaction to ensure uniformity of reaction. The fluidized sand bath is controlled using an Omega temperature controller to ensure temperature stability. The normal charge in the reactor consisted of 1 gram of coal and 2 grams of methanol. After reaction the solid residues were removed from the reactors and ground and then dried in a vacuum oven at 95 degrees Celsius for approximately 90 minutes. The total sulfur was then determined for all the solid residues.

Samples

The three coals used in this study were taken from the Illinois Basin. They include: 1) SIU 1386, from the Herrin No. 6 seam; 2) SIU 647J, from the Brazil Block seam; and 3) SIU 1749, a wash plant mixture of Illinois No. 5 and No. 6. All three coals are high-volatile bituminous in rank with standard vitrinite reflectances of 0.42, 0.49, and 0.79 % respectively. The maceral analysis reveals that coals #1 and #3 are typical midwestern coals composed mainly of vitrinite (82.7 and 85.4 %), while coal #2 has much higher liptinite (11.6 %) and inertinite (22.7%) contents.

RESULTS OF ANALYSIS

Effects of KOH

Prior to standardization the 5% KOH loading was tested against known KOH addition. At low-severity (350 degrees

Celsius, 60 minutes) the presence of KOH shows a slight positive effect on sulfur removal. Under slightly more severe conditions (450-500 degrees Celsius, 30 minutes) the difference between sulfur removal and tests with and without KOH addition increases. The sulfur removals under high-severity conditions (500 degrees Celsius, 60 minutes) shows either no effect or a negative effect of KOH addition. In many cases sulfur removals decrease as reaction times are increased from 30 to 60 minutes. These patterns are independent for the three coals studied and the preparation the coal receives. However, the extent of the reduction is coal dependent. Coal 1 and 2 show a slight reduction in sulfur removal, whereas, coal 3 gives large amounts of sulfur incorporation. This phenomena has been observed previously by Murdie (11). The incorporation is short-lived at moderate-severity and is difficult to pinpoint. At higher severity conditions the degree of incorporation may be permanent. The severe incorporation noted with coal 3 may be experimental coincidence in obtaining the maximum incorporation at the specified temperatures. However, coal 3 did show a consistent linear decrease in sulfur removal as a function of reaction time at 500 degrees Celsius. At 15 minutes reaction time 65% sulfur removal was obtained. At 60 minutes reaction time 6% sulfur removal was obtained. Although incorporation reactions complicate data interpretation, the increase sulfur removals in the presence of KOH were significant enough to standardize on this operation procedure. Thus, most of the data reported is for 5% KOH loadings.

Effects of Sample Preparation

Under mild-severity, micronized coal is less reactive than -60 mesh coal. At moderate-severity the micronized coal tends to be slightly more reactive than the -60 mesh size fraction of the same coal; and at high-severity the micronized coal is substantially more reactive than the -60 mesh size fraction of the same coal.

The data imply that slight oxidation in the fine coal particles retards desulfurization under mild conditions, but mass transport effects are more significant at high-severity. Retardation of sulfur removal under mild desulfurization conditions may be the result of surface oxidation of pyrite particles or oxidation of freshly exposed coal surfaces. The surface oxide on pyrite particles would be expected to be less susceptible to desulfurization at low temperatures. However, at higher temperatures the sulfates would be expected to decompose to SO_x. Sulfur incorporation is more likely to occur at elevated temperatures. The micronized particles allow the product less time to react with components on the pore walls than -60 mesh particles. Thus, micronization reduces the chance of incorporation during the process of product diffusion to the bulk gas. Thus, higher sulfur removals can be observed in the micronized samples. On the other hand, when conditions in the bulk gas favor sulfur incorporation, the smaller particle size of the micronized coal will enhance sulfur incorporation.

Figure 1 demonstrates the effect of the trend in sulfur removal as a function of sample preparation. These results are typical of high-severity SME processing and reflect trends in maximum sulfur removal. The data are reported for samples prepared from coal 1, but the trend is also applicable for sulfur removals from coals 2 and 3. Less sulfur is removed from the -60 mesh size fraction than is removed from the micronized coal; less sulfur is removed from the micronized coal than is removed from the micronized/ demineralized coal; and less sulfur is removed from the micronized/demineralized coal than is removed from the micronized/demineralized/ cesium chloride-floated coal. These data reflect trends that are applicable for all process conditions studied at or above 450 degrees Celsius. The patterns are also independent of the sulfur incorporation phenomena. In other words, if sulfur incorporation is observed for a condition, the magnitude of the incorporation appears to be independent of the sample preparation.

Figure 2 shows sulfur removal under 500 degrees Celsius and 60 minutes reaction time for vitrinite and sporinite maceral concentrates of coal 2. Sulfur removal in the vitrinite and sporinite concentrates are substantially higher than sulfur removal in the micronized coal or the sample prepared by a 1.6g/ml floatation process. The vitrinite and sporinite concentrates contain 86% of the total organic sulfur in the coal. Assuming that none of the sulfur in the other macerals is removed, the results on the vitrinite and sporinite concentrates suggests that 65% of the organic sulfur should be removed in the micronized or floated samples. Since both the float and maceral concentrates contain about the same amount of cesium introduced during the preparation process, catalytic desulfurization effects can be eliminated as a cause for the high desulfurization rates in the maceral concentrates. Thus, the data suggests that other macerals inhibit sulfur removal or trap products of the desulfurization process.

Figure 3 depicts sulfur removal of maceral concentrates at milder experimental conditions. Similar trends are observed. Namely, vitrinite and sporinite concentrates evolve more sulfur than whole or floated coals. Thus, sulfur removals in the vitrinite and sporinite occur at a faster rate as well as reaching a higher maximum. Not enough tests have been conducted on the maceral concentrates to judge sulfur incorporation tendencies.

Figure 3 also contains data for one test conducted on the vitrinite concentrate of coal 1 at a high-severity condition. The sulfur removal in the vitrinite concentrate was found to be higher than the sample prepared by sequential micronization, demineralization, and floatation. The difference in sulfur removal between the maceral concentrate and the floated sample is not as great as the equivalent tests on samples prepared from coal 2. However, the vitrinite concentration in coal 1 is substantially higher than in coal 2. Therefore, the float sample from coal 1 would be expected to be similar to the vitrinite concentrate. The 5% lower sulfur removal in the float sample

indicates a large sensitivity in sulfur removal with variations in maceral concentration.

CONCLUSIONS

The modified DGC method employing a pre-concentration of macerals at specific density cut-points allows for accumulation of a sufficient quantity of pure maceral concentrates for testing the desulfurization properties of individual macerals. The concentration of 10gm aliquots of pure maceral concentrates represents a new advance in coal separation technology. This is the first time that such large quantities of pure macerals have been segregated by any technique.

The conditions under which samples are tested are extremely critical to the extent of sulfur removal. In general, increased temperature increases desulfurization. Also, sulfur removal increases with longer reaction times. The presence of KOH enhances the rate of sulfur removal. Sulfur can be reincorporated from sulfur-containing gaseous products, and KOH enhances the sulfur reincorporation. Some of the sulfur removal may be retarded by incorporation of products during diffusion of product gases through the pore system of the residual coal. Thus, very fine particle sizes are desirable for chemical desulfurization.

The type of sample preparation affects sulfur removal. In general, particle size reduction increases sulfur removal. Demineralization results in increased sulfur removal in subsequent processing. Variations in sulfur removal due to variations in coal properties are observed for the micronized and demineralized coals.

The demineralized coals contain pyrite. Pyrite is removed by floatation at a 1.6gm/ml solution. Floatation produces a very clean coal that is more reactive than the demineralized coal. For float samples, approximately the same maximum desulfurization level is obtained independent of desulfurization process and coal properties.

The float samples demonstrate that organic sulfur is more amenable to desulfurization than was previously thought.

Since high levels of sulfur removal are obtained during pyrolysis, the sulfur removals reported are not an artifact of sample dilution. Furthermore, either pyrite is less reactive than the organic sulfur or the pyrite (or derived products of pyrite) aid in sulfur incorporation reactions. The results suggest the thermal-chemical desulfurization should be preceded by a thorough physical cleaning that removes both pyrite and other coal minerals.

Finally, the main objective of this study was to investigate the desulfurization behavior of individual coal macerals. The sporinite and vitrinite concentrates are more reactive towards desulfurization processes than any of the other

materials that were studied. They also gave the highest desulfurization levels. Since they are more reactive than whole coals or floated samples, the other constituents in the coal matrix must reduce sulfur removals. This phenomena has not been reported previously. It implies that the inertinite macerals may behave in a manner similar to activated charcoal and chemically absorb copious amounts of sulfur during the desulfurization processes. The practical result of this phenomenon is that selection of coals on the basis of maceral composition could be necessary to optimize thermal-chemical desulfurization. Work in this area is continuing at Southern Illinois University at Carbondale.

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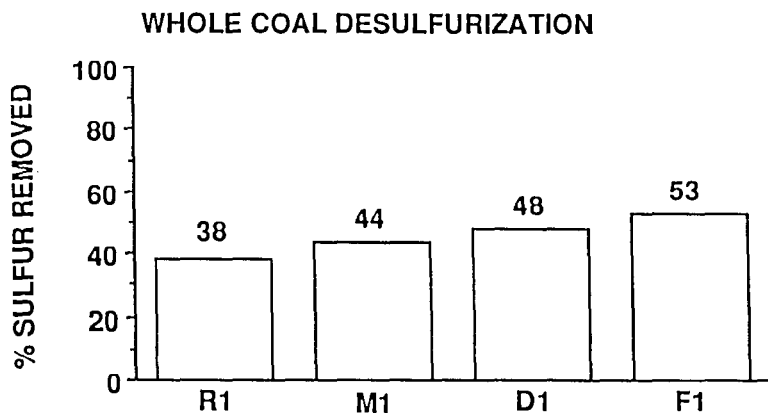


Figure 1. Typical results from a single coal sulfur removal with supercritical methanol extraction at 450 degrees C for 30 minutes showing the effects of pretreatment of the sample. (R = raw, M = micronized, D = micronized and demineralized, F = micronized, demineralized, and floated at 1.6 gm/ml.)

PURE MACERAL DESULFURIZATION

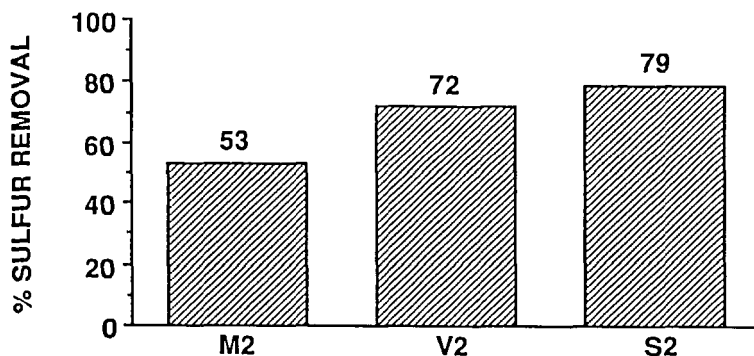


Table 2. Results of sulfur removal with supercritical methanol extraction (SME) on pure maceral fractions from the same coal sample at 500 degrees C for 60 minutes. (M = micronized coal, V = vitrinite, S = sporinite.) It should be noted that the high sulfur removals represent the removal of organic sulfur. Pyritic and sulfate sulfur have been removed earlier.

PURE MACERAL DESULFURIZATION

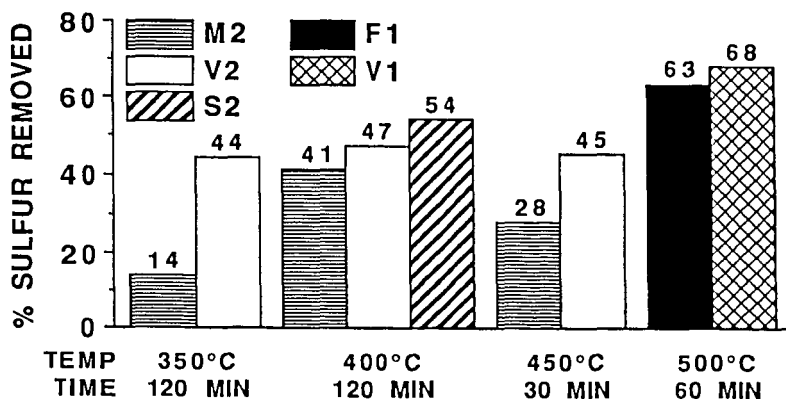


Table 3. Results of sulfur removal with supercritical methanol extraction on pure maceral concentrates. In all cases more sulfur is removed from the macerals than the micronized and/or floated coal. (M2 = micronized coal #2, V2 = vitrinite from coal #2, S2 = sporinite from coal #2, F1 = floated coal #1, and V1 = vitrinite from coal #1.)

SUPERCRITICAL DESULFURIZATION RATES OF WHOLE AND TREATED COALS.

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Introduction

Growing concern over the environmental effects of acid rain has resulted in increased interest in development of precombustion removal of sulfur from coal. Most coals are not in compliance with the recent requirements which call for reduction of sulfur emissions from various fuel sources. Under proposed guidelines, even low sulfur, western bituminous coals require some cleaning to meet new source standards of 1.2 lb. of SO_2 per million Btu's and 90% reduction in sulfur content of the coal on a concentration basis.

Typically, Illinois Basin coals contain more sulfur than coals from other coal bearing regions. In order for typical Illinois coals to meet EPA guidelines, some organic sulfur must be removed, in addition to most of the pyritic sulfur. Almost all Illinois coals contain greater than 1% organic sulfur, with most containing more than 2% [1].

The Department of Mechanical Engineering and Energy Processes at Southern Illinois University is developing a desulfurization process to remove both organic and inorganic sulfur from coal without deleteriously affecting key combustion properties [2]. This process employs alcohols under supercritical conditions. The coal/alcohol mixtures produce a clean solid product with an acceptable sulfur content, a high Btu gaseous product and coal derived liquids.

Supercritical fluid extraction of coals has been reported previously, as a method for the production of liquid fuel products from coal under mild conditions, and as a medium for selective desulfurization of coal [2-4]. Alcohols are expected to exhibit greater solubility for polar organic molecules because of hydrogen bonding and dipole attractive forces. They also provide the opportunity for chemical reactions during the extraction because of the nucleophilicity of the alcohol oxygen and the tendency to act as a hydrogen donor. In addition, enol rearrangements [5] may play a role in desulfurization.

As reported previously [4], different supercritical reaction conditions produced different extents of desulfurization of coals (33.9-65.7%). However this work concentrated on Illinois Coals. The variable desulfurizations probably result from differences in extents of conversion of the pyritic sulfur (to various alteration products, such as pyrrhotite), [4] as well as organic sulfur functionalities (thiophenol, sulfide, and thiophene)

to light gases such as dimethylsulfide, hydrogen sulfide and methylmercaptans. Although the exact mechanism of the methanol/sulfur functionality reactions are not known, the reactions are believed to be complex, involving hydrogen donation by the alcohol, as well as nucleophilic substitutions.

The overall objective of this study was to gain a better understanding of the supercritical alcohol/coal desulfurization process. Initial development of the supercritical desulfurization process utilized a batch reactor system [4]. Recently, microreactor system has been developed, which is similar to tubing bombs developed by Neavel [6], for coal liquefaction studies. This new system has several advantages over the batch reactor system and approximates more closely the operating conditions of the continuous reactor. Using the microreactor system, the heating and cooling times were reduced compared with those required for the batch reactor. This reduction of heating and cooling time, from 60-120 minutes in the batch reactors to 2-3 minutes in the microreactors, is anticipated to give a better understanding of the reaction kinetics under supercritical conditions. The microreactors are designed to provide a uniform temperature within the reactor and allow precise measurements of temperature. Previous optical characterization of the batch reactor residues suggested that mass and/or heat transfer resistance might be present in the batch system [4].

This paper describes the desulfurization of various coals in supercritical methanol. The objective of the study is to determine the effect of coal properties and treatment of coals on desulfurization rates in supercritical methanol. The effects of KOH addition on desulfurization rates is discussed. Other treatments such as physical cleaning and acid demineralization are reported in an associated paper [7].

Experimental

The eight samples studied in this investigation were obtained from the Argonne Premium Coal Sample Bank. The analysis are reported in Table 1. These samples ranged in rank from Lignite to Low Volatile Bituminous and ranged in Sulfur contents from 0.5 to 5.0% on a dry basis. The values reported in Table 1 were calculated from as received basis as reported by Dr. Vorres, the manager of the sample bank.

For some experiments, the coal was treated with KOH. In these experiments, the coal was soaked overnight in a 5% KOH solution of alcohol.

The reaction of coal with methanol was carried out using a microautoclave system. The apparatus consisted of a 10 cc. stainless steel microautoclave linked to a metering valve and a quick disconnect fitting by high pressure tubing. The reactor system was attached to an automatic shaker supported above a fluidized sand bath. The shaker allowed the autoclave to be agitated during reaction to ensure uniformity of reaction. The fluidized sand bath was temperature stability. Pressure was monitored by an Omega pressure transducer connected to the reactor through a two way valve.

Supercritical Reaction

The microautoclaves were first flushed with nitrogen to remove any oxygen present. The reactors were then charged with coal (1 g.) and methanol (2 g.). Further pressurized flushings with nitrogen were carried out to ensure the removal of oxygen after the microautoclave had been sealed. The valve was opened after successive flushed to release the pressurized nitrogen. The charged microreactors were then attached to an automatic shaker held above a sand bath, as shown in Figure 1. The fluidized sand bath was the raised, so as to fully submerge the reactor in the fluidized sand, which had been preheated to the desired temperature. The shaker was then switched on for the desired reaction time (30, and 60 minutes).

Following reaction, the sand bath was lowered and the reactors removed from the shaker. The reactors were vented by slowly opening the metering valve. After the valves had been opened fully for approximately one minute, the reactors were then quenched in a water bath.

The solid residues were removed from the reactors, ground, and then dried in a vacuum oven at 95°C for approximately 90 minutes. The reactors were cleaned after each run, using acetone in an ultrasonic bath to remove tarry residues. Total sulfur analysis was carried out on all of the solid residues. Desulfurization can be calculated on a concentration or weight basis. The results in this paper are reported on a concentration basis. A concentration basis would be used by the EPA if the 90% removal requirements were to be applied. The weight basis is useful in understanding sulfur incorporation and coal vaporization. The two basis can be calculated as follows:

$$\begin{aligned}\%S \text{ Removed}(\text{conc.}) &= (\%S \text{ Raw Coal} - \%S \text{ Product}) / \%S \text{ Raw Coal} \\ \%S \text{ Removed}(\text{wt. \%}) &= (\text{wt. S Raw Coal} - \text{wt. S Product}) / \text{wt. S Raw Coal}\end{aligned}$$

DESULFURIZATION OF COALS OF VARIOUS RANKS

Desulfurization results obtained on the Argonne Premium samples are listed in Table 2. The coals are listed in approximate rank order from left to right. Results are listed for a moderately severe temperature of 400 C, and a high severity temperature, 450°C. Reaction times of 30 and 60 minutes were studied. Results are also listed for tests conducted with and without KOH present.

In general, desulfurization results decrease from left to right indicating a tendency for sulfur to be less removable as rank increases. For example, the data listed for no KOH, 400°C, and 30 minutes of reaction time shows that the sulfur removal in the lignite is an order of magnitude greater than for the low volatile bituminous coal. This relationship can be seen in Figure 1. Since more weight loss is obtained in the lower rank coals, the relationship is more pronounced when the weight percent basis is used. The scatter in the data shown in Figure 1 also decreases when data are viewed on the weight percent basis. However, there is some variability in the relationship within the high volatile rank range even when weight factors are taken into account. Muchmore et al[3] have reported that the Organic to pyritic sulfur ratio has an effect on desulfurization of Ill.

basin coals and Hippo et al[7] have reported that physical cleaning increases subsequent desulfurization response. Thus variation in total sulfur, pyritic to organic sulfur ratio, and mineral content and composition might explain some of the observed variations.

Results from the tests conducted at 400°C at 30 minutes reaction time yield information on rates of sulfur removal. Two additional factors need to be considered. These factors are the maximum desulfurization obtainable and the selectivity of the sulfur removal. Although the test conducted thus far can not answer these questions entirely, they do shed light on the problems each coal has in obtaining the desired 90% removal level. For example the lignite coal yielded a 70-75% reduction in sulfur on a concentration basis and 85-89% reduction on a weight basis for the 450°C tests without KOH addition. But, this was obtained at 48% weight loss. Energy balances have not been conducted, but the 48% weight loss must represent a significant loss of energy to the vapor phase. This is not necessarily a detriment since the liquid in gases could be sold after they were cleaned. But, the weight losses complicate the analysis of the data and the determination of the optimum desulfurization conditions.

For 5 of the eight coals examined, the maximum sulfur removal in the absence of KOH occurred at 450°C and 30 minutes of reaction time. The other three coals yielded higher sulfur removals on a concentration basis at 400°C. The difficulty in specifying conditions at which maximum sulfur removals will occur arises from many factors. The major factor is that sulfur removals on a concentration basis can decrease with increase reaction time and temperature. Examples of this can be seen throughout Table 2. The decrease in the sulfur removal can occur for two reasons. One, incremental weight losses results in low selectivity towards additional sulfur removal and an increase in the selectivity toward hydrocarbon removal. For example, results at 450°C for 30 and 60 minutes reaction time in the absence of KOH for coal 6 shows a decrease in the concentration of sulfur removed even though on a weight basis the total sulfur removal has increased from 35 to 39%. The second reason for decreases in the sulfur removal on a concentration basis is due to incorporation of sulfur as has been reported previously[8]. For example, at 60 minutes of reaction time for 400°C and 450°C in the presence of KOH; coal 5 decreases in sulfur removal from 43% to -2% on a concentration basis. The weight % sulfur removed also decreases from 45% to 3%.

Both of these factors appear to be somewhat dependent on coal rank. The low rank coals appear to be more susceptible to loss of sulfur removal due to loss of selectivity than the high rank coals. For example the subbituminous coal in the absence of KOH shows a decrease in the sulfur removal at 450°C between the 30 and 60 minutes of reaction time despite an increase in the total sulfur removed. Furthermore when the lower rank coals show some decrease in the total weight of sulfur removed; it is usually small in magnitude. The higher rank coals show the exact opposite trend. When a decrease in sulfur removal on a concentration basis is observed it is always as a result of a decrease in the weight of sulfur removed. In addition as rank increases, the relative amount of sulfur that is incorporated back into the coal residue increases. Thus, Rank appears to be one factor that influences selectivity of the sulfur removal and the incorporation of the sulfur.

The above observation may be the result of the experimental conditions employed. As has been reported previously, the extent of the sulfur incorporation is extremely condition sensitive[8]. In addition, equilibrium considerations may be dominant in the system. If so, then total sulfur in the vapor phase might contribute to the sulfur incorporation. Other factors might include the composition of the minerals present and the reactions that the minerals undergo during the extraction process. Pyrite and other minerals might catalyze the incorporation phenomena. The incorporation might be temporary as observed by Murdie et al[8] or at the high severity the incorporation may be permanent. The cause of the incorporation is not understood. It may be associated with phase changes reducing the solubility of the sulfur compounds in the supercritical vapor, or it may be due to the reaction of sulfur compounds in the bulk vapor phase with coal radicals created by the thermal processing of the coal. At mild severity the sulfur may remain active towards removal but at high severity the incorporated sulfur may crosslink and become inactive toward the alcohol.

EFFECT OF KOH ADDITION

The effect of KOH can also be seen in Table 2. At almost every condition KOH increases sulfur removal. The few results where KOH does not increase sulfur removal is where extensive sulfur incorporation is noted. Since KOH does not effect the global activation energy[8], the increase sulfur removals must be due to physical effects. One possibility is that KOH may function as a crosslinking agent. This is supported by the well known tendency of KOH to reduce fluidity, agglomeration, and swelling. Or KOH may serve as a cracking catalysts providing increase amounts of sulfur sites for reaction. In order to have no effect on the activation energy, the cracking reaction must be much faster than the sulfur removal reactions. This idea is supported by the large effects that KOH has on coals 5 and 6. The data also suggest that KOH plays a role in the incorporation of sulfur. The extent of sulfur incorporation is much greater in the presence of KOH. This may be simply that KOH provides a larger concentration of sulfur compounds in the vapor phase at the conditions that incorporation occurs. Or, the KOH may play a direct role in adding sulfur to coal free radicals and thus providing a higher probability for sulfur to be affixed by crosslinking.

CONCLUSIONS

This study has shown that:

- 1) Desulfurization is rank dependent.
- 2) Other coal properties effect desulfurization.
- 3) KOH increases sulfur removal and sulfur incorporation.
- 4) Maximum desulfurization is difficult to access.
- 5) Sulfur removal is condition dependent.
- 6) Sulfur removal selectivity varies throughout the process.
- 7) Optimization for maximum selectivity and removal requires an understanding of sulfur incorporation kinetics and mechanism as well as removal mechanisms and kinetics.

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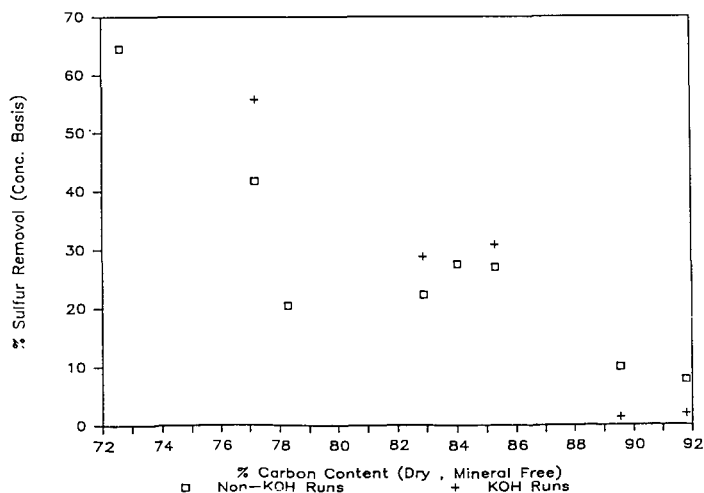


Figure 1. DESULFURIZATION IS A FUNCTION OF RANK: The data in the graph is for supercritical methanol extraction at 400°C and 30 minutes reaction time. Both KOH and Non-KOH runs indicate that sulfur is difficult to remove as rank increases.

TABLE I

Properties of Coals* Used in Supercritical Methanol Extraction Tests

COAL	UPPER FREPORT	WYODAK	ILL	NO.6	PITTSBURGH NO.8	POCAHONTAS NO.3	BLIND CANYON	LEWISTON STOCKTON	BEULAH ZAP
SAMPLE NO.	1	2	3		4	5	6	7	8
(dry)									
ULTIMATE									
ANALYSIS									
CARBON	75.46	69.35	65.2		75.6	86.6	74.1	65.1	67.15
HYDROGEN	4.72	2.42	4.82		5.34	4.48	5.7	4.38	7.89
NITROGEN	1.40	1.05	1.19		1.49	0.93	1.30	1.03	0.92
SULFUR	2.49	0.66	5.05		2.25	0.61	0.59	0.70	0.78
OXYGEN	2.83	17.57	6.04		5.88	2.48	13.65	8.98	16.73
(by diff.)									
PROXIMATE									
ANALYSIS									
ASH	13.10	8.95	17.7		9.44	4.90	4.68	19.81	6.53
VOLATILE									
MATTER	27.6	33.95	30.92						
SULFUR									
FORMS									
SULFATE	0.01	0.007	0.008		0.01	0.003			
PYRITE	1.98	0.12	2.78		1.39	0.178			
ORGANIC	0.50	0.54	2.26		0.85	0.427			
CALORIC									
VALUE	13,362	11,646	10,290						
MINERAL									
MATTER**	15.73	10.17	21.31		11.32	5.62	5.40	22.5	7.5

*Properties of Argonne Coals Supplied by Karl Vorres except Sulfur Contents which were determined at SIUC.

**PARR Formula.

TABLE II

Coal No. Rank	DESULFURIZATION OF ARGONNE PREMIUM SAMPLE COALS IN SUPERCRITICAL METHANOL									
	8 Lignite	2 Sub-bit	3 High Vol	6 High Vol	7 High Vol	4 High Vol	1 Med Vol	5 Low Vol		

REACTION CONDITIONS
TEMPERATURE TIME
°C MIN.

NO KOH ADDITION

400	30	65	42	22	21	28	27	10	8
400	60	74	47	21	8	30	32	24	17
450	30	75	50	28	19	34	24	29	3
450	60	70	48	26	14	32	28	33	7

KOH ADDITION

400	30		56	29			34	1	10
400	60		61	28	56		32	24	45
450	30		42	35	72		32	37	19
450	60		54	30	66		12		3

THE CONVERSION OF ORGANIC SULFUR IN COAL TO SULFATE USING PERCHLORIC ACID

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ABSTRACT

Based upon our previous research in which the variable oxidizing power of perchloric acid (HClO_4) was used to determine directly the organic sulfur in coal, it was hoped that this property of HClO_4 could be also used to determine different forms of organic sulfur in coal. This preliminary investigation into the usage of HClO_4 to delineate between various organic sulfur forms was based on model compounds. Dibenzothiophene, benzothiophene, diphenyl sulfide, 2-naphthalenethiol, dibenzyl disulfide, and dioctyl sulfide were oxidized in a Bethge apparatus with HClO_4 of varying concentration and boiling point. To insure complete sulfur recovery, gases produced during the reaction were captured in a trap containing hydrogen peroxide. Sulfate was then measured nephelometrically, after precipitation as barium sulfate, in the residual HClO_4 solution and in the peroxide trap. No appreciable amount of sulfate was measured for the aromatic compounds until a temperature of 170°C or higher was reached. However, for dibenzyl disulfide and dioctyl sulfide, large amounts of sulfate were measured in the trap, even at lower temperatures. The volatility of these two compounds may be a contributing factor in their high conversion to sulfate.

INTRODUCTION

A method for the direct determination of the sulfur forms in coal has been developed which takes advantage of the selective oxidizing ability of perchloric acid (1). In that method, sulfate sulfur was extracted from a coal sample with a boiling perchloric acid solution having a boiling point of 120°C . At the boiling point of 120°C , perchloric acid is a non-oxidizing acid. If any sulfidic sulfur was present, it was converted to hydrogen sulfide and absorbed in the trap containing 15 percent hydrogen peroxide. The residue from the 120°C reaction was reacted with a perchloric acid solution at a boiling point of 155°C . At this temperature, perchloric acid begins to have some oxidizing power (2). Thus, pyritic sulfur was converted to sulfate and a sulfur-containing gas which was trapped in hydrogen peroxide. The residue from the 155°C reaction was reacted with a 9:1 mixture of concentrated perchloric and phosphoric acids boiling at 205°C . At this temperature, perchloric acid is a powerful oxidizing agent (2), converting organic sulfur to sulfate and a sulfur-containing gas which was trapped in hydrogen peroxide. Total sulfur was determined by reacting another coal sample with the 9:1 mixture of perchloric and phosphoric acids. Sulfate was determined turbidimetrically in the perchloric acid solution and in the peroxide trap after precipitation as barium sulfate. Sulfur recoveries were good and the results for sulfur forms compared well with the results obtained using the ASTM procedure (3) on the same coals. The development of this method was

based on a series of perchloric acid oxidations performed on coal-derived pyrite and the Charming Creek coal from New Zealand in which almost all of the sulfur was organic (4).

The present study was undertaken for two reasons. The first was to further validate that organic sulfur was not oxidized appreciably at 155°C. The second reason was to investigate the possibility of delineating between various organic sulfur forms by taking advantage of the considerable variation in the oxidizing ability of perchloric acid. It was hoped that different sulfur functionalities would react at different temperatures above 155°C to produce sulfate and/or sulfur-containing gases. To attain these objectives, several sulfur-containing organic compounds were oxidized with perchloric acid solutions ranging in boiling point from 155°C to 203°C (concentrated perchloric acid). The model compounds subjected to oxidation were dibenzothiophene, benzo thiophene, diphenyl sulfide, 2-naphthalene-thiol, dibenzyl disulfide, and dioctyl sulfide.

EXPERIMENTAL

Dibenzothiophene, benzo thiophene, diphenyl sulfide, 2-naphthalene thiol, and dioctyl sulfide were obtained from Aldrich Chemical Company. Dibenzyl disulfide was obtained from Columbia Chemical Company. All reagents were used as received. All reactions were run in a modified Bethge apparatus described previously by McGowan and Markuszewski (4). The Bethge apparatus was designed to maintain a constant boiling mixture. The system was fitted with a trap containing 15 percent hydrogen peroxide to collect sulfur-containing gases and convert them to sulfate.

A Note on Safety. The use of perchloric acid alone as an oxidizing agent for organic materials always poses a hazard. In this study, all reactions were performed in a hood and behind an explosion shield. For each sample, reactions were performed at the lower temperatures first. For reactions at 203°C, small samples were reacted to minimize the possibility of an explosion. In the course of this study, a small fire occurred during the reaction of a 0.3-mL sample of dioctyl sulfide at 190°C and for a 0.1-mL sample of dioctyl sulfide reacted at 203°C. The fires were contained in the reaction vessel and no glassware was broken. The authors recommend that extreme care be taken any time perchloric acid alone is used as an oxidizing agent for organic materials.

Reaction Procedure. For the oxidations, the following procedure was followed. A perchloric acid solution was added to the Bethge apparatus and the boiling point adjusted to the desired temperature. By varying the initial amount of perchloric acid solution added, a final volume of approximately 50 mL was obtained. The perchloric acid solution was allowed to cool. In the case of dibenzyl disulfide and dioctyl sulfide, the 9:1 mixture of perchloric acid and phosphoric acid was used instead of only concentrated perchloric acid for the reaction at 205°C. A weighed sample of the solids or a pipetted sample of the liquids was placed in the Bethge apparatus. The mass of the liquid

samples was calculated by using handbook densities. A gas absorption bottle containing 100 mL of 15 percent hydrogen peroxide was attached to the top of the Bethge apparatus. Nitrogen was used as the purge gas. The reaction vessel was heated to the stable reaction temperature, and the reaction was allowed to proceed for 1.5 hrs. After the heat was removed, the system was purged for an additional 30 min. with nitrogen. The solution in the absorption bottle was boiled to insure oxidation of all the sulfur to sulfate and to reduce the volume to approximately 25 mL. The solution was transferred to a 50-mL volumetric flask and diluted to mark. After cooling, the perchloric acid reaction mixture was filtered. The filtrate was transferred to a 250-mL volumetric flask and diluted to mark.

Sulfate in the trap and the filtrate was determined by precipitation with barium and spectrophotometric measurement of the turbidity of the resultant barium sulfate suspension. The procedure used was described by Markuszewski et al. (5) and modified by McGowan and Markuszewski (4). Since some of the filtrates contained a solid material, the solutions were allowed to sit at least overnight and the sample used in the analysis was pipetted from the supernatant liquid. Since most of the filtrates were also colored, the absorbance of the sample without barium chloride added was measured and subtracted from the absorbance of the test solutions. In the case of analysis of the filtrates, perchloric acid was added to the standards to approximate the acid concentration of the filtrates.

RESULTS AND DISCUSSION

The results for the oxidation of model compounds in which the sulfur is attached directly to an aromatic ring appear in Tables 1-4. The results were very similar. Only insignificant amounts of sulfate were measured in products from the reactions carried out at 155°C. For the reactions at 170°C, a significant amount of sulfate was measured for 2-naphthalenethiol, while the remaining aromatic compounds still produced only insignificant amounts. With increasing temperature, the amount of measured sulfate increased linearly, and sulfur recovery was complete for the reactions carried out at 203°C. For the aromatic materials, most of the sulfate was found in the filtrate as the temperature increased above 170°C.

Table 1. Results for the oxidation of dibenzothiophene
(Theoretical=17.4% sulfur)

Boiling Point (°C)	Sample Weight (g)	Sulfur in Trap (% Samp.)	Sulfur in Filtrate (% Samp.)	Total Sulfur (% Samp.)	Sulfur Recovered (% of Theor.)
155	0.3062	0.09	0.30	0.39	2.2
170	0.3095	0.00	0.00	0.00	0.0
180	0.3129	2.23	0.18	2.41	13.8
190	0.2956	1.43	7.05	8.48	48.7
203	0.2956	2.21	15.29	17.50	100.5

Table 2. Results for the oxidation of benzothiophene
(Theoretical=23.9% sulfur)

Boiling Point (°C)	Sample Weight (g)	Sulfur in Trap (% Samp.)	Sulfur in Filtrate (% Samp.)	Total Sulfur (% Samp.)	Sulfur Recoverd (% of Theor.)
150	0.5024	0.46	0.27	0.73	3.1
155	0.4993	0.59	0.34	0.93	3.9
170	0.5000	0.16	0.44	0.60	2.5
180	0.5065	1.21	6.07	7.28	30.4
190	0.5000	2.53	11.80	14.33	60.0
203	0.0623	3.68	19.70	23.38	97.9

Table 3. Results for the oxidation of diphenyl sulfide
(Theoretical=17.2% sulfur)

Boiling Point (°C)	Sample Weight (g)	Sulfur in Trap (% Samp.)	Sulfur in Filtrate (% Samp.)	Total Sulfur (% Samp.)	Sulfur Recovered (% of Theor.)
150	0.3354	0.34	0.28	0.62	3.6
155	0.3354	0.09	0.44	0.53	3.1
170	0.3354	0.00	0.00	0.00	0.0
180	0.3354	1.91	1.55	3.46	20.1
190	0.3354	2.12	6.86	8.98	52.2
203	0.1115	1.40	14.60	16.00	92.9

Table 4. Results for the oxidation of 2-naphthalenethiol
(Theoretical=20.0% sulfur)

Boiling Point (°C)	Sample Weight (g)	Sulfur in Trap (% Samp.)	Sulfur in Filtrate (% Samp.)	Total Sulfur (% Samp.)	Sulfur Recovered (% of Theor.)
155	0.3118	0.13	0.00	0.13	0.7
171	0.3022	1.67	0.80	2.40	12.0
180	0.3138	2.63	8.52	11.15	55.8
190	0.2961	1.98	11.74	13.72	68.6
203	0.0996	1.24	20.67	21.91	109.6

The results for the oxidation of compounds in which the sulfur was attached to an aliphatic carbon appear in Tables 5 and 6. For these compounds, significant amounts of sulfate were found in the peroxide traps for reactions at all the temperatures tested. For dibenzyl disulfide, 87-108% of the theoretical amount of sulfur was recovered at

155-205°C. Over 80 percent of the sulfur contained in dibenzyl disulfide was found in the gas trap for every reaction except that at 205°C. Lesser amounts of sulfate were measured for reaction products from dioctyl sulfide. For the reactions at 155°C and 170°C, the peroxide traps had foul, nauseating odors. This suggested that the sulfur-containing gases trapped were thiolic in nature and did not exist as an oxidized form of sulfur. The implication is that oxidation occurred on the carbon portion of the molecule, forming smaller, more volatile organosulfur compounds which escaped and were subsequently trapped. This was especially true for dibenzyl disulfide, containing the reactive benzyl carbon. The amounts of sulfate measured in the filtrates for dioctyl sulfide were similar to the amounts measured for the aromatic compounds. For dibenzyl disulfide, lesser amounts of sulfate were measured in the filtrate.

Table 5. Results for the oxidation of dibenzyl disulfide
(Theoretical=26.0% sulfur)

Boiling Point (°C)	Sample Weight (g)	Sulfur in Trap (% Samp.)	Sulfur in Filtrate (% Samp.)	Total Sulfur (% Samp.)	Sulfur Recovered (% of Theor.)
155	0.3099	21.78	0.86	22.64	87.3
170	0.3068	22.16	1.17	23.90	90.0
181	0.3050	22.20	2.18	24.38	93.8
190	0.3000	22.33	3.43	25.76	98.8
205	0.1090	9.48	18.82	28.30	108.8

Table 6. Results for the oxidation of dioctyl sulfide
(Theoretical=12.4% sulfur)

Boiling Point (°C)	Sample Weight (g)	Sulfur in Trap (% Samp.)	Sulfur in Filtrate (% Samp.)	Total Sulfur (% Samp.)	Sulfur Recovered (% of Theor.)
155	0.2526	3.72	0.00	3.72	30.0
170	0.2526	4.08	0.00	4.08	32.9
181	0.2526	6.02	2.97	8.99	72.5
190	0.2526	7.24	4.34	11.56	93.2
205	0.0842	1.41	12.56	13.97	112.6

Benzothiophene, diphenyl sulfide, and 2-naphthalenethiol were soluble in perchloric acid, giving clear solutions. Only very small amounts of char formed during the reactions at 170°C to 190°C. The odor of naphthalene was noted in the filtrates of the reaction of 2-naphthalene-thiol at 170°C and 180°C. A black char formed during the reaction of dioctyl sulfide at 155°C, 170°C, and 180°C. The color of the filtrates from the above reactions ranged from yellow at 155°C to orange and brown at 170°C and 180°C, respectively, and back to clear at 203°C.

During the oxidation of dibenzyl disulfide, a purplish-black, gummy solid, representing from 60 to 90 percent of the sample mass, formed at temperatures from 155°C to 190°C. The color of the filtrates indicated that some new compounds were formed at temperatures below 203°C. The filtrate was orange-pink at 155°C, light orange at 170°C, orange with a green tint at 181°C, dark brown at 190°C, and colorless at 203°C.

Dibenzothiophene was insoluble in perchloric acid, and unreacted dibenzothiophene was recovered from reactions carried out at 180°C and below. A different, yellow solid was formed at 190°C. This solid material was analyzed by Fourier transform infrared spectroscopy and mass spectrometry. Three series of compounds were identified in the solid. The major series consisted of chlorinated dibenzothiophene sulfones containing from one to seven chlorine atoms. A second series consisted of chlorinated dibenzothiophenes containing from one to eight chlorine atoms. A minor series of chlorinated compounds for which the base was dibenzothiophene plus three oxygen atoms was also indicated. No solid was recovered from the reaction carried out at 203°C.

CONCLUSIONS

Aromatic sulfur compounds are not oxidized to sulfate or a sulfur-containing gas by perchloric acid having boiling points of 170°C or lower. At higher temperatures, aromatic sulfur compounds apparently are oxidized by perchloric acid first to sulfones and chlorinated sulfones, then to sulfonic acids and finally to sulfate. Volatile sulfur-containing gases are not produced by this oxidation sequence. However, for aliphatic sulfur compounds, the carbon portion is apparently oxidized at lower temperatures, resulting in the formation of volatile sulfur-containing compounds which are trapped in hydrogen peroxide.

For analysis of a coal containing aliphatic sulfur near the end of a chain, it is possible that some of the sulfur measured after reacting the coal at 155°C could be due to organic sulfur, thus causing a positive error in the measurement of pyritic sulfur. However, during previous oxidation reactions of several different coals, no odor has ever been noted around the trap of the reaction carried out at 155°C, indicating that this possibility is probably low. Since a difference has been noted in the oxidation of aromatic sulfur and aliphatic sulfur compounds, the possibility of distinguishing between the two forms exists, and further investigation is warranted.

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DESULFURIZATION OF COAL BY PHOTO-OXIDATION

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Abstract

Desulfurization of coal by oxidative methods has been investigated by several workers. These techniques primarily involve selective oxidation of organic sulfur to sulfoxide and sulfones, followed by thermal decomposition of the oxidation product.

In this study, photo-oxidation of sulfur in coal is investigated. Finely divided coal samples, suspended in solvent(s), are exposed to radiation using ultraviolet and xenon lamps. The coal samples are next subjected to hydrolysis to remove the oxidized sulfur from the coal matrix. The effect of wave length, light intensity, slurry concentration, and duration of exposure is studied. The maximum desulfurization achieved is about 42%.

Introduction

The U.S. has about one-third of the world's known coal reserves. But coal is difficult to mine, expensive to transport and heavily polluting. The pollution is mainly due to the presence of mineral matter (ash) and sulfur which gives rise to the formation of fly ash and sulfur dioxide. Fossil energy research, development, and demonstration strategy is to develop a wide variety of coal utilization techniques that are clean, efficient and conserve resources. Industry can then choose promising processes which will eventually be commercialized. However, there is one serious limitation to increased consumption of coal namely, sulfur dioxide pollution caused by its direct combustion. There is still a need for an efficient and inexpensive coal desulfurization technique which utility companies could readily use. In this paper, desulfurization of coal using a photo-oxidation technique is discussed.

Scientific Rationale for Photo-Desulfurization of Coal

Coal is a complex mixture of organic and inorganic compounds in which the organic matrix comprises most of the coal weight. Organic coal matrix can be viewed as a complex macromolecular structure containing the classical organic functional groups such as carbonyl and hydroxyl, aromatic and heterocyclic ring units, and aliphatic bridges. The organic sulfur in coal can be categorized into one of the functionalities such as thiol, sulfide, disulfide, thiophene, benzothiophene, and dibenzothiophene.

Desulfurization of coal has been investigated by several workers (1,2). They have used techniques such as oxidation (3-6), chlorinolysis (7-8), electrolysis (9), etc. All these methods essentially oxidize sulfur in coal. There are other methods reported in the literature involving hydrogenolysis, hydrolysis, etc. It is observed that among the organic sulfur functionalities, removal becomes increasingly difficult in the order thiolic < sulfide <

disulfide < thiophenic < benzothiophenic < dibenzothiophenic. As the complexity of the sulfur containing functionality increases the selectivity of desulfurization, without affecting the rest of the coal matrix, becomes difficult. For example, the selectivity of hydrodesulfurization is reduced whenever the n-electrons of sulfur are in resonance with π -electrons as in the cases of thiophene, benzothiophene, etc. This leads to competing hydrogenolysis of the carbon-carbon bonds since the energies of carbon-sulfur and carbon-carbon bonds become practically identical due to resonance (10). It has been reported that atmospheric weathering leads to desulfurization of coal which can be due to the combined effect of air oxidation and photo-oxidation. However, the authors have not presented any mechanism or photonic role for this process (6).

It has been suggested that accompanying the oxidation of the sulfur to sulfone, the bond energy between the carbon and the sulfur is reduced on the average by 5.2 kcal/mole for aliphatic sulfides and by 11.8 kcal/mole for aromatic sulfides and thiophenes. Thus, the selectivity of decomposition at the sulfur-carbon bond is increased (3).

Oxidative desulfurization of coal has been studied by several workers (1-8). These methods primarily involve two steps: (1) selective oxidation of organic sulfur to sulfoxide and sulfones as shown below and (2) thermal decomposition of the oxidation product expelling sulfur dioxide.

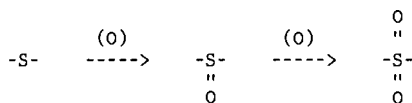


Photo-oxidation of Sulfur in Coal

No work is reported on the photochemical oxidation of coal. It is important to understand how the coal molecule would react in the presence of light and air. Coal due to its strong absorption of the entire visible spectrum has black color. It is also well known that coal has a complex aromatic structure with polyaromatic nuclei capable of absorbing light in the visible region. Attached to these are the sulfur atoms. The n-electrons on sulfur can resonate with the aromatic π -cloud. Hence, in the presence of light the n, π^* transition is also feasible which would affect the bonding properties of sulfur. This might lead to either electron deficient sulfur linkage or formation of diradical or free radicals. Due to the complexity of coal structure it is difficult to theoretically predict the exact course of reaction from the excited state.

There is enough literature evidence that oxygen in air attacks the organic sulfur compounds photochemically (11). Extending the mechanism of photo-oxidation of sulfur compounds to coal, two courses of reaction can be predicted. One of them could be the formation of free radical/diradical center at sulfur from the excited coal molecule and subsequent oxidation and hydrogen abstraction leading to oxidized sulfur functionalities such as sulfonic acid. The second one would be the attack of sulfur center by excited molecular oxygen, namely, singlet oxygen, if the reaction conditions are conducive to the production of

singlet oxygen. Either of these mechanisms would cause the formation of sulfoxides, sulfones or sulfonic acids depending upon the reaction conditions. Hence, it is safe to predict that the organic sulfur functionalities in coal could be oxidized in the presence of oxygen and visible light.

By this photo-oxidation treatment the sulfur in coal would remain in an oxidized form. The next step would then be to eliminate the oxidized sulfur from the coal matrix. This can be achieved by subjecting the photo-oxidized coal to hydrolysis. This procedure is reported to be used in other chemical desulfurization techniques also. It is envisaged that most sulfur removed by this technique as sulfonic, sulfurous or sulfuric acid or their derivatives would be organic in nature (12).

Experimental Set-up and Procedure

Finely crushed coal is suspended in 95% ethanol and kept agitated by bubbling oxygen at such a rate that the coal particles are not allowed to settle down. Also, oxygen bubbling would facilitate the removal of sulfur by oxidation. The coal slurry is subjected to photolysis in an internally lighted reaction vessel. In some experiments methylene blue is used as a sensitizer for the production of singlet oxygen. The photo-oxidized coal is washed thoroughly with ethanol to remove the dye and the ethanol is separated by centrifugation. Next, the coal is dried at 110°C for 8 hours. A portion of the photo-oxidized coal is subjected to hydrolysis either in boiling water or by refluxing with solutions of HCl or NaOH. Reference coal is also hydrolyzed with water, acid or base under the same conditions employed for photolyzed coal in order to study the effect of photolysis. The samples are analyzed for their sulfur contents.

In a second set of experiments, coal samples suspended in solvent(s), are exposed to high intensity light using an apparatus as shown in Figure 1. The other details remain the same as for experiments conducted in an internally lighted reaction vessel.

Results and Discussions

Details of the experimental conditions and results are presented in Table I through Table III. Effect of wave length on sulfur reduction is presented in Table I, showing a photonic advantage of about 35% when coal samples are exposed to radiation of wavelength 254nm as compared to 23% for 300-600nm. In both cases coal samples are subjected to hydrolysis in 1N NaOH medium. It is to be noted that same % sulfur reduction is obtained for water hydrolysis at 254nm. On the other hand, a photonic advantage of only 5% is achieved when coal samples are exposed to wave length 300-600nm and subjected to water hydrolysis.

Effect of methylene blue, as a sensitizer, on sulfur reduction when added to coal samples suspended in 95% alcohol and exposed to wave length 300-600nm is presented in Table II. No change in sulfur reduction is observed.

Effect of light intensity on sulfur reduction in coal is presented in Table III. The coal samples are suspended in water, 1N NaOH, and 95% alcohol and exposed to xenon light (800 watts) for 4 hours duration. Coal slurry is maintained at 8.3%. In spite of this high slurry concentration the photonic advantage is observed to be 16.5%, 22.5%, and 20.5% for water, 1N NaOH, and 95% alcohol, respectively. It may also be noted that coal samples are exposed for 4

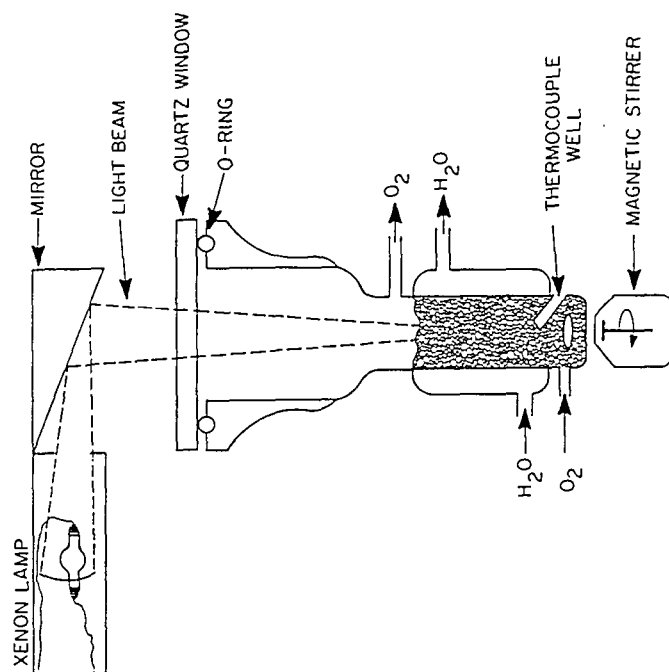


FIG. 1 HIGH INTENSITY PHOTOREACTOR ASSEMBLY

Table I
Effect of Wavelength on Sulfur Reduction

Parameters	S.N. 1	S.N. 2	S.N. 3	S.N. 4
Coal	Ill#6 Bituminous	Ill#6 Bituminous	Ill#6 Bituminous	Ill#6 Bituminous
Slurry Concentration	2%	2%	2%	2%
Particle Size	44 micron	44 micron	44 micron	44 micron
Solvent	95% ethanol	95% ethanol	95% ethanol	95% ethanol
Reactor	internal	internal	internal	internal
Sensitizer	none	none	none	none
Radiation	300-600nm	254nm	300-600nm	254nm
Light Intensity	450 watts	100 watts	450 watts	100 watts
Reaction Time	16 hr	16 hr	16 hr	16 hr
Hydrolysis Duration	reflux 8 hr	reflux 8 hr	reflux 8 hr	reflux 8 hr
Hydrolysis Medium	water	water	1N NaOH	1N NaOH
% Sulfur Reduction				
Dark Hydrolysis	6.1%	6.1%	6.5%	6.5%
Light Hydrolysis	11.5%	41.9%	30.0%	41.8%
Photonic Advantage	5.4%	35.8%	23.5%	35.3%

hours only. An experiment is also conducted with light intensity of 450 watts using the internal photo-reactor (S.N.4) for coal slurry of 8.3% exposed for 4 hours duration. A photonic advantage of only 10% is obtained. An advantage of using high intensity light is clearly observed.

Conclusions

The results of this study show that there is a reduction in sulfur of about 24% when coal particles are subjected to 300-600nm radiation. It is also observed that coal slurry concentration can be increased and time of photolysis reduced at high intensity light exposure. The use of ultraviolet light (254nm) shows higher sulfur reductions compared to when coal samples are exposed to radiation of wavelength 300-600nm.

Acknowledgment

This study was funded by the Solar Energy Research Institute, U.S. Department of Energy, Golden, Colorado 80401. The use of high intensity photoreactor assembly at the Department of Chemistry, University of Houston, Houston, TX is also gratefully acknowledged.

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Table II
The Effects of Methylene Blue on Sulfur Reduction (12)

Parameters	S.N. 1	S.N. 2	S.N. 3	S.N. 4	S.N. 5	S.N. 6
Coal	111#6 Bituminous	111#6 Bituminous	111#6 Bituminous	111#6 Bituminous	111#6 Bituminous	111#6 Bituminous
Slurry Concentration	2%	2%	2%	2%	2%	2%
Particle Size	74 micron	44 micron	44 micron	44 micron	44 micron	44 micron
Solvent	95% ethanol	95% ethanol	95% ethanol	95% ethanol	95% ethanol	95% ethanol
Reactor	internal	internal	internal	internal	internal	internal
Sensitizer	Methylene Blue	Methylene Blue	Methylene Blue	none	none	none
Radiation	300-600nm	300-600nm	300-600nm	300-600nm	300-600nm	300-600nm
Light Intensity	450 watts	450 watts	450 watts	450 watts	450 watts	450 watts
Reaction Time	16 hr	16 hr	16 hr	16 hr	16 hr	16 hr
Hydrolysis Duration	reflux 6 hr	reflux 6 hr	reflux 6 hr	reflux 8 hr	reflux 8 hr	reflux 8 hr
Hydrolysis Medium	water	IN HCl	IN NaOH	water	IN HCl	IN NaOH
Sulfur Reduction						
Dark fly rolysis	4.5%	14.9%	4.2%	6.1%	6.9%	6.5%
Light Hydrolysis	12.0%	17.4%	27.8%	11.5%	9.1%	30.0%
Photonic Advantage	7.4%	3.4%	23.7%	5.4%	2.2%	23.5%

Table III
Effect of Light Intensity on Sulfur Reduction

Parameters	S.N. 1	S.N. 2	S.N. 3	S.N. 4
Coal	Ill#6 Bituminous	Ill#6 Bituminous	Ill#6 Bituminous	Ill#6 Bituminous
Slurry Concentration	8.3%	8.3%	8.3%	8.3%
Particle Size	44 micron	44 micron	44 micron	44 micron
Solvent	water	1N NaOH	95% ethanol	95% ethanol
Reactor	High Intensity	High Intensity	High Intensity	internal
Sensitizer	none	none	none	none
Radiation	Xenon	Xenon	Xenon	300-600nm
Light Intensity	800 watts	800 watts	800 watts	450 watts
Reaction Time	4 hr	4 hr	4 hr	4 hr
Hydrolysis Conditions	reflux 8 hr	reflux 8 hr	reflux 8 hr	reflux 8 hr
Hydrolysis Medium	1N NaOH	1N NaOH	1N NaOH	1N NaOH

% Sulfur Reduction

Dark Hydrolysis	6.5%	6.5%	6.5%	6.5%
Light Hydrolysis	23.0%	29.0%	27.0%	16.2%
Photonic Advantage	16.5%	22.5%	20.5%	9.7%

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MIGRATION OF SULFUR BETWEEN ORGANIC AND INORGANIC PHASES DURING HYDRODESULFURIZATION PROCESSES¹

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The co-occurrence of organic sulfur and iron sulfides in high-sulfur coal and their interrelationships are suggested to play an important role in the design and effectiveness of methods for precombustion desulfurization. The mobility and interconversion of pyritic and organic sulfur forms can be both advantageous as well as disadvantageous. Iron catalysts have been reported to exhibit high activity in coal gasification (4). More extensive studies have been done regarding the role of iron sulfides in hydroliquefaction in which pyrite is transformed to pyrrhotite and H₂S which will catalyze hydroliquefaction around 380°C (5). Studying this phenomena in more detail, with coal model compounds, showed that 316 stainless steel was a radical scavenger in the H₂S promoted radical chain cleavage of the model compounds, while pyrrhotite and pyrite decreased the reaction rate to a lesser extent (6-9). The formation of sulfur-containing organic compounds during hydrogen sulfide promoted liquefaction leading to reduction of overall desulfurization is undesirable. This is especially disadvantageous if either inorganic sulfur or easily desulfurized organic sulfur compounds are converted to less easily desulfurized thiophenic sulfur. The identification of organosulfur compounds in coal using reductive, oxidative, or metallic reagents continues to be studied with the obvious limitations in distinguishing original coal structures from secondary products formed during reactions of organic compounds with minerals, especially during pyrolysis conditions (10-18).

In the course of investigation of the non-isothermal hydrodesulfurization of model organic sulfur compounds in a coal-like environment with and without troilite, it was found that some of the non-thiophenic sulfur from the organic compounds was absorbed by troilite (1). This observation suggested that during hydrodesulfurization the organic sulfur had migrated to the inorganic phase. As the temperature was raised, more H₂S evolved from the sample with troilite, suggesting reevolution by pyrrhotite to troilite conversion.

The purpose of this study was to use isotopic labeling to determine the mechanism of incorporation of sulfur into troilite. One possibility, as suggested by the formation of pyrrhotite confirmed by Mössbauer spectroscopy, is that the H₂S produced from the organic compound was transferred to the inorganic phase, and then as the temperature was raised, H₂S evolution occurred from the troilite. Another possibility was that a direct reaction between the troilite and the organic compound took place, forming an intermediate followed by H₂S evolution from this intermediate as the temperature was raised. The fate and H₂S evolution profile from the labeling of the mobile organic sulfur group has been studied in an effort to distinguish possible mechanisms and demonstrate the role of troilite in this process.

MATERIALS

Two ³⁴S labeled compounds 2-(thiomethyl)dibenzothiophene (2) and 4-(thiomethyl)-dibenzothiophene (3) were prepared from dibenzothiophene (1) using our previously reported methods as shown in Scheme 1 (19). Compounds 2 and 3 gave spectral data in agreement with their structural assignments, including high resolution mass spectral confirmation. Compound 2 gave m/z 232.0179 for C₁₃H₁₀³²S³⁴S (calculated 232.0181) and compound 3 gave m/z 232.0140.

EXPERIMENTAL

The coal-like mixture was prepared by grinding together 8 mg of compound 2 or 3 and 60 mg of charcoal (previously degassed by heating to 680°K *in vacuo*) with or without 80 mg of troilite. The mixture was placed in a pyrex tube placed in a furnace. Hydrogen was passed through the tube at a flow of 55 mL/min while heating at 3°/min from 523°K to 700°K. The evolving gases were analyzed for the ratio of H₂³²S to H₂³⁴S as the temper-

ature was raised using a quadrupole mass spectrometer attached to a split off the gas outlet. The residue was extracted with CH_2Cl_2 to recover the organic desulfurized compound, 2- or 4-methyldibenzothiophene and the remaining residue subjected to the combustion-precipitation sequence previously reported for isotopic analysis of coal pyrolysate chars (1,20).

RESULTS AND DISCUSSION

The hydrodesulfurization of 2-(thiomethyl)dibenzothiophene(2) with and without troilite gave a total H_2S evolution profile as a function of temperature shown in Figure 1. The major process producing H_2S was the desulfurization of the thiomethyl group occurring between 523°K and 600°K while the thiophenic group began to slowly desulfurize around 725°K. In the presence of troilite, the total H_2S evolution was similar, except less evolved between 523°K and 550°K, while slightly more evolved between 550°K, and 600°K. The amount of H_2^{34}S evolved from 2 is expected to follow the same profile between 523°K and 550°K. If some $^{34}\text{H}_2\text{S}$ migrated into the troilite, then at the higher temperatures, as the H_2S reevolved from the pyrrhotite, the H_2^{34}S would be diluted by isotopic mixing, resulting in decreased H_2^{34}S evolution relative to H_2^{32}S evolution. A corresponding increase in the ^{34}S isotopic composition of the char would then be expected. If no mixing occurred, the H_2^{34}S evolution profile would be expected to follow the same pattern as the total H_2S , with no increase found in the char.

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Scheme 1

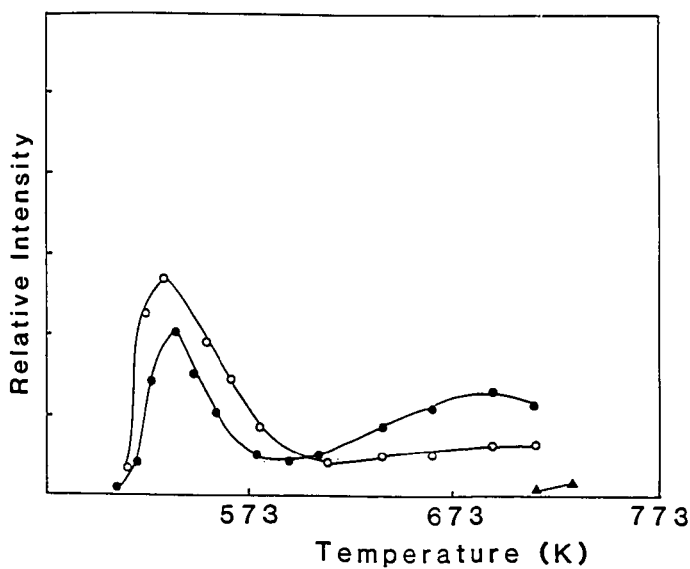
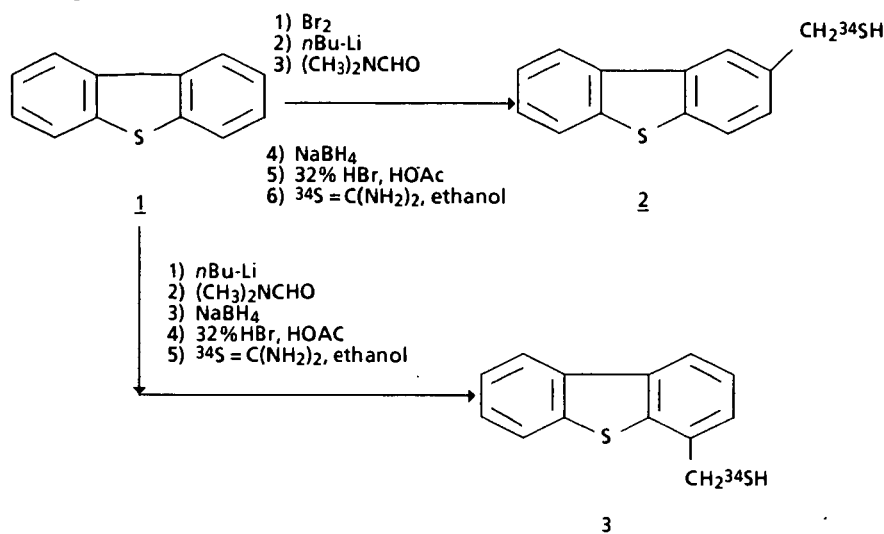


Figure 1. Rate of H₂S evolution as a function of temperature for compound 2 and dibenzothiophene at a heating rate of 3°K/min: O, compound 2 without troilite; ●, compound 2 with troilite; ▲, dibenzothiophene without troilite.

HYDRODESULFURIZATION OF A SPANISH LIGNITE

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The objective of this work is to investigate catalytic hydrodesulfurization (HDS) reactions of lignite under mild conditions. The reactions are conducted in a single stage in the absence of a donor solvent. The lignite being studied is Mequinenza (Spanish) lignite, which has the exceptionally high sulfur content of 12.9% (daf basis). Most of the sulfur in this lignite is present as organic sulfur, the organic sulfur content being 11.6% daf. Since about 90% of the total sulfur is organic, physical coal cleaning methods designed to remove pyritic sulfur are not applicable to this lignite.

On a commercial scale, the role of a hydrodesulfurization operation would be, ideally, to remove the sulfur as H_2S leaving a desulfurized coal or char having a heating value comparable to that of the feedstock. Under the HDS reaction conditions the formation of some hydrogen-rich liquids is inevitable; these liquids could be used either directly or after a second HDS step as raw materials for petrochemical processes. Our research was not primarily concerned with the process development, but rather focused on the chemistry of the HDS reactions of the lignite.

Transition metal catalysts, particularly containing cobalt, molybdenum, nickel, or tungsten, have been widely used in coal and coal liquids processing at high temperature and high pressure conditions, both with and without donor solvents. Sulfides of these metals have activity as hydrodenitrogenation and HDS catalysts. For example, the HDS activities of molybdenum and cobalt/molybdenum sulfide catalysts have been investigated for HDS of thiophenes (1,2). Currently there is extensive interest in HDS catalysts using both alumina and carbon supports (3-8). Zinc chloride has also been shown to catalyze the removal of sulfur from coal-derived compounds (9).

There appear to be no current studies of coal HDS in the absence of donor solvent. In the absence of a solvent, supported heterogeneous HDS catalysts could not be used. Consequently, we have impregnated the lignite with catalyst precursors which subsequently form the active catalysts, dispersed throughout the lignite, at reaction conditions. Collateral research at Penn State has explored the use of dispersed catalysts and absence of solvent for liquefaction (e.g., 10,11) but as far as we are aware the work reported here is the first such study for the principal purpose of HDS.

EXPERIMENTAL

The Mequinenza lignite samples were obtained from the Instituto Nacional del Carbon y Sus Derivados, Oviedo, Spain. On a daf basis the lignite contains 64.81% C, 5.72% H, 12.93% S. The forms of sulfur (dry basis) were 1.17% pyritic, 0.20% sulfate, and 9.20% organic. The ash content was 20.40% (dry basis). The lignite samples were crushed to -60 mesh in a glove box under oxygen-free nitrogen and subsequently vacuum freeze dried to less than 1% moisture. The dried samples were stored under nitrogen.

The general procedure for catalyst impregnation was to dissolve the requisite quantity of the catalyst precursor (a water-soluble salt of the desired metal) in sufficient distilled water to give a water:coal ratio of 1:1. A slurry of the lignite in this solution was stirred for at least two hours. After stirring, the excess water was removed by vacuum freeze drying to less than 1% moisture. Normally, enough lignite for a complete series of experiments would be impregnated in one batch and stored under nitrogen. For experiments with molybdenum, the catalyst precursor was ammonium tetrathiomolybdate, which was prepared by bubbling H_2S through an aqueous solution of ammonium heptamolybdate for 30 minutes.

HDS reactions were conducted in microautoclave reactors (tubing bombs) of 25 - 30 ml capacity. The reactors were pressurized with hydrogen and immersed in a preheated fluidized sand bath. The reactors were oscillated vertically through 2.5 cm at 200 cycles/min for the desired reaction time. For this work initial (cold) hydrogen pressures of 1000 and 1500 psi, reaction temperatures of 250 - 350°C, and reaction times of 0.5 - 4.0 hr were used.

After reaction, the yields of CO , CO_2 , C_{1-4} hydrocarbons and H_2S were determined by GC. The reactor contents were washed with solvent (chloroform, tetrahydrofuran (THF), and ethanol were tested) into an alundum thimble and extracted under nitrogen in a Soxhlet apparatus for 20 - 24 hr. Solvent was removed from the extracts in a rotary vacuum evaporator. The extracts and insoluble residue were dried in a vacuum oven for 18 - 20 hr at 100°C before weighing. Yields of extract and insoluble residue were directly determined; total gas make was calculated by difference.

RESULTS AND DISCUSSION

Total Sulfur Removal

To establish a set of baseline conditions, a set of standard conditions was established using ammonium tetrathiomolybdate catalyst precursor, 1000 psi H_2 pressure, 0.5 hr reaction time, and THF as the extraction solvent. The catalyst loading was equivalent to 1% by weight of molybdenum. The results obtained with these conditions at five temperatures are summarized in

Table 1 below.

TABLE 1. Results of HDS with Standard Test Conditions, dry basis

Temp., °C	Conversion	Extract	H ₂ S Yield	Total S Removed
250	12.8%	12.6%	-	9.57%
275	13.8%	13.6%	-	13.1%
300	20.8%	19.1%	0.18%	23.9%
325	38.0%	33.0%	1.4%	47.7%
350	68.1%	53.6%	7.1%	77.2%

A marked shift in the reaction chemistry occurs in the temperature range of 300 - 325°C. First, below 300° the catalyst has essentially no effect on the reaction. For example, in reaction at 275° without catalyst impregnation but at otherwise identical reaction conditions, a conversion of 10.3% and total sulfur removal of 16.2% were observed; these results are very close to those shown in Table 1 for the catalytic experiment. By contrast, at 350° in the absence of catalyst, the conversion is only 33.7% and total sulfur removal, 48.1%. Two alternative explanations may be proposed to explain these observations: The active form of the catalyst, which is presumed to be molybdenum disulfide, may not yet have formed from the precursor at the relatively low temperature reaction conditions. Alternatively, the MoS₂ catalyst may not be active for HDS in this system below 300°.

A second aspect of the change in reaction chemistry at the higher conditions is the form in which sulfur is ultimately being removed from the system. At or below 300° essentially all of the sulfur is removed in the form of organosulfur compounds which are taken out with the extract. At the higher temperatures, most of the sulfur is removed as H₂S. Specifically, at 350° 84% of the sulfur lost from the lignite appears as H₂S, whereas at 300° only 7% (of a smaller total amount of sulfur removed) appears as H₂S. In a reaction at 350° in the absence of catalyst, the proportion of the sulfur removed as H₂S is 33%.

In this system at temperatures above 300°, the catalyst is performing two roles. First, it facilitates the breakdown of the coal structure, as shown by the higher extract yields in the catalytic vs. non-catalytic experiments. Second, it facilitates HDS, as shown by the much higher proportion of the total sulfur removed being lost as H₂S in the catalytic experiments (e.g., 84% vs 33% at 350°). There are two mechanisms by which the total HDS may be proceeding under these conditions. One possible mechanism is the direct reaction of hydrogen with sulfur functional groups in the lignite to form H₂S. The second is the liquefaction of the lignite to form sulfur-rich liquids which then undergo a subsequent HDS in situ to produce the H₂S. (A third option is that both mechanisms are proceeding simultaneously.) At present we do not have enough data to suggest which, if either, is the predominant mechanism.

Catalyst Screening

Although a 77% reduction in total sulfur is encouraging, the reaction conditions, particularly the temperature, needed to achieve this reduction are severe. Thus it is of interest to evaluate other potential catalysts to determine whether greater sulfur reduction, lower reaction temperatures, or both, are possible. This section is a brief review of results obtained with dispersed catalysts other than the standard MoS_2 .

Cobalt and cobalt/molybdenum. The catalyst precursor for cobalt was $\text{Co}(\text{NO}_3)_2$; for the cobalt/molybdenum system, a solution of cobalt acetate and molybdenum oxalate. At 300° , 1000 psi H_2 , and 0.5 hr reaction time the results show slight improvement compared to the MoS_2 and non-catalytic systems. The results are summarized in Table 2. The catalyst loadings were 1% Mo and 0.6% Co by weight daf, which gives equal atomic amounts of the two metals.

TABLE 2. HDS by Cobalt and Cobalt/Molybdenum Catalysts, 300°C , 1000 psi H_2 , 0.5 hr; dry basis.

<u>Catalyst Precursor</u>	<u>Conversion</u>	<u>Extract</u>	<u>Total S Removed</u>
None	17.7%	15.7%	26.7%
$(\text{NH}_4)_2\text{MoS}_4$	20.8%	19.1%	23.9%
$\text{Mo}(\text{C}_2\text{O}_4)_2$	27.1%	23.3%	28.9%
$\text{Co}(\text{NO}_3)_2$	25.8%	23.5%	28.7%
$\text{Mo}(\text{C}_2\text{O}_4)_2/\text{Co}(\text{OAc})_2$	24.3%	23.9%	25.9%

Tungsten sulfide. The precursor was ammonium tetrathio-tungstate. The catalyst loadings were 1.9 and 5.7% by weight daf, giving the same tungsten loading in the lignite as would be equivalent on an atomic basis to 1 and 3% by weight Mo. At 300° , 1000 psi H_2 and reaction time of 1 hr, the conversion and extract yield were both below the values obtained under the same conditions without catalyst: conversions of 16.0 vs 19.1% and extract yields of 13.0 and 16.7%, respectively. However, reaction in the presence of the tungsten sulfide catalyst generally gave the highest concentrations of hydrogen sulfide in the gaseous products. At the reaction conditions of 300° , 1000 psi H_2 and 1 hr, the gas yields were 3.1% for molybdenum sulfide catalyst and 3.0% for the tungsten sulfide, but the hydrogen sulfide in these gases was 1.05 and 3.0%, respectively, essentially a three-fold increase. These results suggest that the mechanism of tungsten sulfide catalysis may be different from that of molybdenum sulfide. We plan further work with tungsten sulfide in both hydrodesulfurization and liquefaction studies.

Zinc chloride. The results obtained at 275° , 1000 psi H_2 and 2 and 4 hr residence times are very similar to those obtained under the same conditions using molybdenum sulfide catalyst (with comparable metal loadings on an atomic basis). Under these

conditions the only advantage of the zinc chloride catalyst in comparison to molybdenum sulfide is that the zinc chloride does not introduce additional sulfur into the system, though of course the introduction of chloride may be undesirable in its own right. Mobley and Bell found that zinc chloride promotes desulfurization of aliphatic sulfides and disulfides via H_2S evolution (9). In our work, the H_2S formation in the presence of zinc chloride catalyst was of the same magnitude as from experiments without catalyst addition. There are several explanations for this observation. The organosulfur groups in the Mequinenza lignite may be of the aromatic sulfide, thiophene, or benzothiophene type, which are not susceptible to hydrocracking at our reaction conditions in the presence of zinc chloride. The liberated sulfur may react with the zinc to produce zinc sulfide, which would remain with the THF-insoluble residue. Also, our experiments were at temperatures about 50° below other work done with this catalyst (9).

CONCLUSIONS

It is possible to achieve significant reduction in the sulfur content of this remarkable lignite by HDS in the presence of a molybdenum sulfide catalyst at temperatures of 350° . A distinct change in HDS chemistry occurs around 325° . Below that temperature, most of the sulfur removed from the lignite is removed as organosulfur compounds in liquid products, whereas at 325° and above most of the sulfur is removed as H_2S . The use of zinc chloride and cobalt or cobalt/molybdenum catalysts did not appear to offer any significant advantages over the use of molybdenum sulfide. In terms of total sulfur reduction, the same is true of tungsten sulfide. However, the fact that tungsten sulfide catalysis significantly increases H_2S formation relative to comparable experiments with molybdenum sulfide suggests that the chemistry of HDS over tungsten sulfide is worthy of further investigation.

ACKNOWLEDGEMENTS

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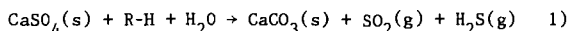
Using X-ray Methods to Evaluate the Combustion Sulfur Minerals and Graphitic Carbon in Coals and Ashes

David L. Wertz and Leo W. Collins

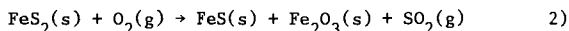
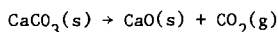
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INTRODUCTION

Coals are complex mixtures of vastly different materials whose combustion kinetics may well exhibit symbiotic effects. Although the sulfur oxide gases produced during the combustion of coals may have a variety of sources, they are frequently caused by the thermal degradation of inorganic minerals to produce "acid rain"; i.e.,



or



Since many of the minerals involved either as reactants or products in coal combustion produce well defined x-ray powder diffraction (XRPD) patterns, the fate of these minerals may be followed by measuring the XRPD patterns of combustion products.

Coal 1368P, a coal with an unusually high pyrite (FeS_2) fraction, has been the subject materials in our investigations of the fate of the inorganic minerals during combustion. These studies include measuring the fate of pyrite and of graphitic carbon in coal 1368P under varying combustion conditions. The results discussed below were obtained by standard XRPD methods (1).

EXPERIMENTAL

The analysis of coal 1368P, as furnished by PSOC (2), is provided in Table I along with some specialized information which resulted from our x-ray analysis.

Table I. A Definition of Coal 1368P

A. Rank: high volatile bituminous A	
B. Proximate Analysis:	
Ash:	16.7% (a)
Fixed Carbon:	40.0%
Volatile Matter:	37.1%
Moisture:	6.2%
C. Ultimate Analysis	
Carbon:	60.3%
Hydrogen:	4.4%
Nitrogen:	1.4%
Sulfur:	9.6% (FeS_2)
Oxygen:	1.3% (SeO_2)
D. Results of USM X-ray Measurements	
μ^* :	17.2 cm^2/g by XRA
minerals in ash:	Fe_2O_3 and SiO_2 by XRPD
major elements:	Fe, S, and Si by XRF
(a) The ash weight is not necessarily the minerals fraction in the non-combusted coal.	

Each finely powdered sample of coal 1368P was combusted in a Lindberg Single Zone Furnace which approximates a stoker furnace. Each coal sample was weighed prior to and after combustion to determine its mass loss. Each partially combusted product was finely powdered and then loaded into our automated x-ray diffractometer. An x-ray powder diffraction pattern was obtained by measuring the counts accumulated in a ten second interval collected at increments of $d2\theta = 0.05^\circ$.

RESULTS AND DISCUSSION

The x-ray powder diffraction patterns of several partially combusted products from coal 1368P are shown in figure 1. These products were produced by one minute combustions with no air flow through the combustion chamber and at several different combustion temperatures. Key diffraction peaks characterizing quartz (Q), pyrite (P), hematite (H), and troilite (T) are indicated, as is the large, broad hump due to the amorphous material(s) in each sample.

QUARTZ PEAK. Previous results have shown that the 3.343 \AA peak of quartz is not measurably affected by the mild combustion conditions used in these experiments (3), so this peak has been used as a reference in the interpretation of each XRPD pattern. The increase in the intensity of the quartz peak indicates an increase in the abundance of quartz, which is due to the removal of the volatile and moisture fractions from the coal (4). Shown in Table II is the intensity of the quartz peak measured in the XRPD patterns shown in figure 1.

Table II. Absorption Corrected Intensity of the 3.343 \AA Quartz Peak Measured in the XRPD Patterns of the Combustion Products

Combustion Temperature	Peak Area
coal	2183
400	2545
600	2762
800	3326
1000	4072
1200	4017
1400	3809 (a)

(a) Thermal degradation may be beginning to occur at this temperature.

Comparison of the areas of the quartz peaks in the XRPD patterns may be used to calculate the loss of the volatile components during each partial combustion. Shown in Table III is the mass loss caused by each combustion protocol calculated from our XRPD analysis and compared to the mass loss measured by normal gravimetric methods. The excellent agreement indicates that the XRPD patterns are sufficiently accurate to use for the semi-quantitative analysis of the pyrite and of the graphitic carbon in the combustion products of coal 1368P.

Table III. Mass Loss Caused by Combusting coal 1368P for One Minute With Zero Air Flow

Combustion Temperature	Mass Loss	
	Gravimetric	Our XRPD
400	17.1%	16.6%
600	20.9%	21.0%
800	35.3%	34.4%
1000	44.8%	46.4%
1200	46.1%	45.6%

By using the ratio of the intensity 2.40 Å pyrite peak/intensity 3.34 Å quartz peak the pyrite abundance in each sample may be determined without the necessity of adding an "external standard" to each combustion sample. Using the graphitic maximum/quartz peak ratio allows a similar determination of the graphitic carbon retained in each combustion product. The uncertainty in each analysis is $\pm 5\%$.

PYRITE ANALYSIS. Although several of the diffraction peaks characterizing FeS_2 are in themselves suitable for the analysis methods we have developed, the 2.40 Å peak is not, in these complicated XRPD patterns, overlapped by diffraction peaks due to other materials. For that reason the 2.40 Å peak has been used in the subsequent analyses as a measure of the weight fraction of pyrite in the combustion products. Shown in figure 2 are the ratios of the 2.40 Å pyrite peak intensity/3.34 Å quartz peak intensity in each combustion product for which both the air flow and the temperature were varied. From the measurement of the pyrite peak in each combustion product, the percent pyrite reacted may also be calculated (fig. 2). These data indicate that the thermal degradation of pyrite begins at $T > 600^\circ\text{C}$, with all of the pyrite reacted at $T = 1200^\circ\text{C}$.

GRAPHITIC CARBON ANALYSIS. Shown in figure 3 is the ratio of the area under the broad amorphous maximum which measures the graphitic carbon (5) to the quartz peak area in each mixture. Also shown is the percent graphitic carbon reacted for each of the combustion products. These data indicate that only a small portion of the graphitic carbon reacts, even under the most severe combustion conditions employed in these experiments.

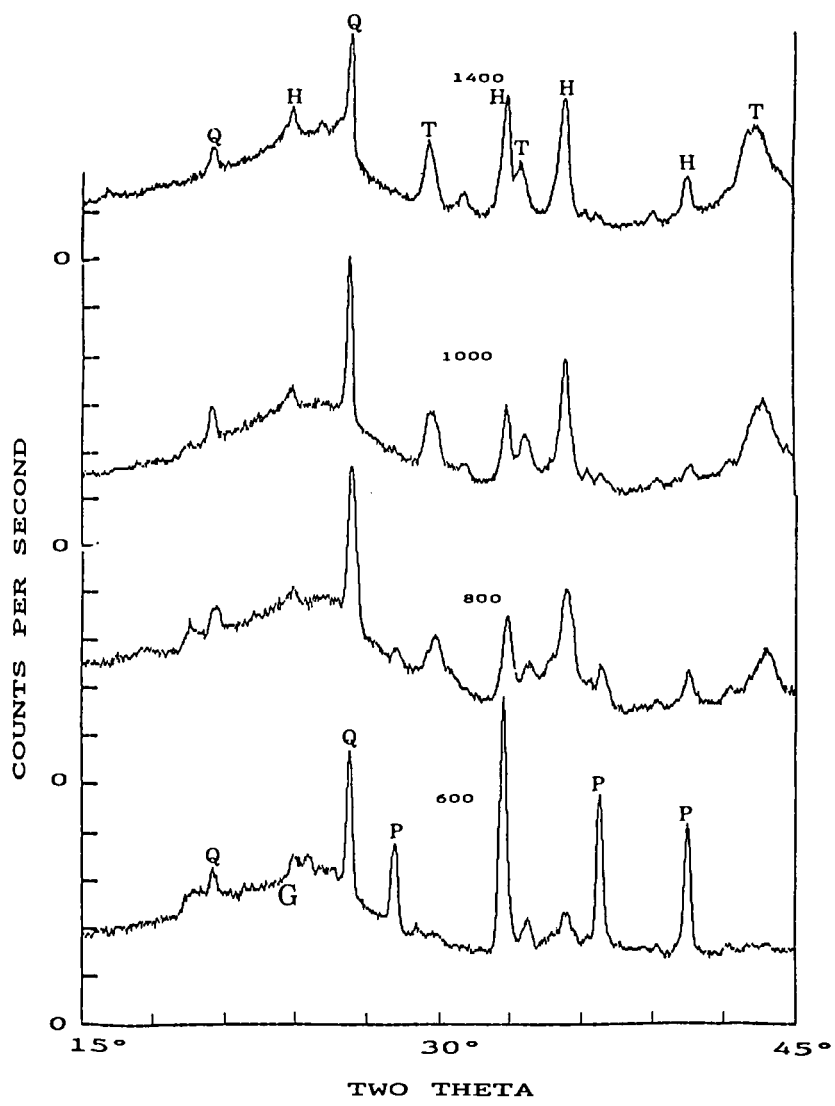
CONCLUSIONS

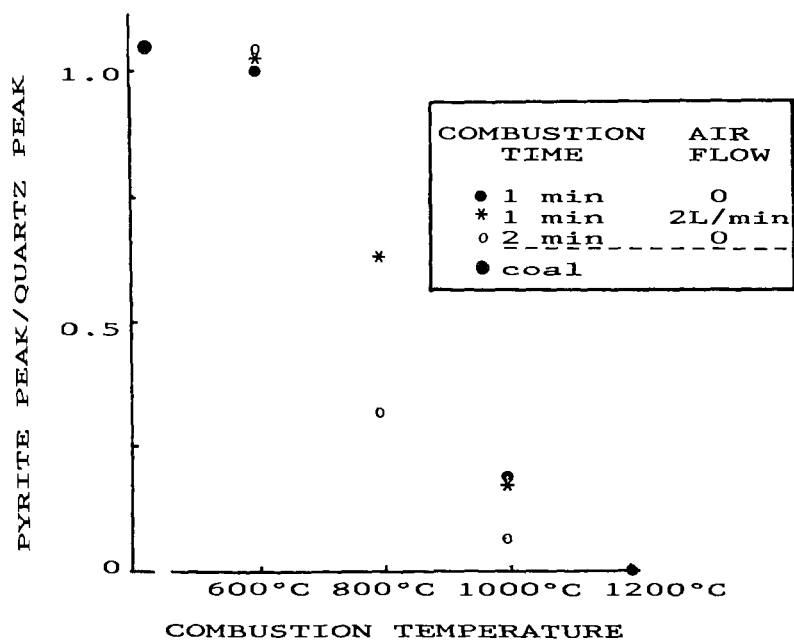
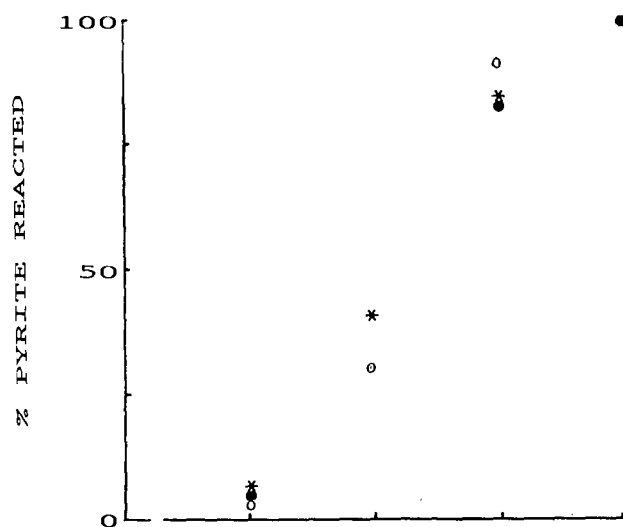
By using quartz in a sample of the powdered coal as the "internal reference" and our XRPD ratio method, the fate of pyrite and of graphitic carbon in combustion processes may be determined. These XRPD data may be manipulated to minimize the ratio of reacted pyrite/reacted graphitic carbon by measuring the pyrite and graphitic carbon retained in each combustion product.

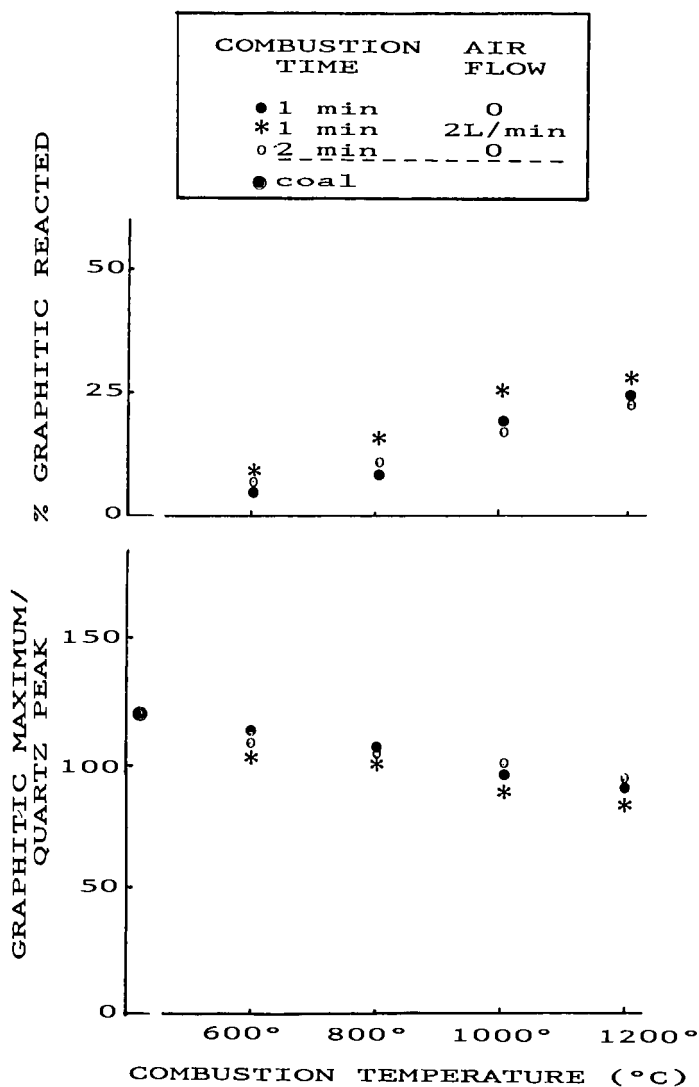
The same XRPD data may be used to determine the combustion conditions at which the volatile and moisture fractions of the coal are completely removed and to evaluate the quality of the combustion product for commercial usage.

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INFLUENCE OF COAL TYPE AND PYROLYSIS TEMPERATURE ON SULFUR DISTRIBUTION IN PRODUCTS DURING DEVOLATILIZATION

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ABSTRACT

During coal devolatilization, the coal sulfur is distributed into solid, liquid, and gaseous products depending on the type and quantity of the coal sulfur and the processing conditions (e.g., temperature, pressure, and heating rate) used. In this study, a series of coals was devolatilized at a relatively low temperature in a fixed-bed reactor in an inert atmosphere. The distribution of sulfur in solid, liquid, and gaseous products was monitored. Influence of peak devolatilization temperature on sulfur distribution in products was determined for a high-volatile bituminous coal (Pittsburgh No. 8). The sulfur content of the pyrolysis liquids generated at 500°C correlate well with the total coal sulfur. The total sulfur of the char can be correlated with the pyritic sulfur content of the coal. Total gaseous sulfur content (sum of H_2S and COS) increases with the increase in pyritic or organic sulfur of coal but direct correlations are poor. An increase in pyrolysis temperature increases the total gaseous sulfur yield. Based on sulfur distribution data for about 25 coals, models have been developed to correlate the sulfur yield in products with the total sulfur of the feed coal.

INTRODUCTION AND OBJECTIVES

A fundamental understanding of the physical and chemical transformations of coal sulfur which occur during pyrolysis is essential for effective utilization of the large reserve of coal available in the United States (1). Work at the Morgantown Energy Technology Center (METC) demonstrated that a relatively high-quality liquid fuel (low sulfur, high H/C) can be produced by low-temperature devolatilization of coal (2,3). Coal devolatilization is a key step in various conversion processes including gasification, combustion, and liquefaction. The organic and inorganic constituents of coal (including sulfur) undergo significant changes during devolatilization. The extent of these changes depend on the peak pyrolysis temperature, heating rate, gas atmosphere, and most importantly, coal type. The objective of this study was to investigate the distribution of coal sulfur into gaseous, liquid, and solid products that occurs during devolatilization of coal of various types.

BACKGROUND

Influence of Coal Type on Sulfur Evolution

Numerous factors influence the mechanisms of sulfur release during the pyrolysis of coals of various types. Some excellent reviews on the sulfur chemistry of coal are available (4-11). However, with the exception of a few limited studies (10,12,13), relatively little has been reported on the influence of coal type on sulfur release during devolatilization, especially at relatively low temperatures (500 to 600°C). This temperature region is where significant changes in coal structure occur. Furthermore, very few correlations between the sulfur in coal and its distribution in the products and evolution rates are available in the literature.

It is generally accepted that three forms of sulfur occur in coal (8,14): (a) organic sulfur (an integral part of coal structure), (b) pyritic and/or marcasites (generally discrete particles or "lumps"), and finally, (c) sulfates (as salts of calcium or iron). Sulfates are not usually present in large quantities in raw

coal. However, significant amounts can be formed if the coal has been weathered (i.e., oxidized). The type and distribution of organic sulfur vary widely in a complex manner in different coals. Roughly 40 to 70 percent of the organic sulfur of a coal is in thiophene structure (and its derivatives). The remaining 30 to 60 percent is present as thiols (R-SH), sulfides (R-S-R'), and disulfides (R-S-S-R'). Thiophenes are hetero-aromatic compounds with the sulfur as part of an aromatic ring. In an aryl sulfide, the sulfur is linked to an aromatic ring. In cyclic sulfides, the sulfur is part of a nonaromatic ring. Sulfides are usually present as aryl sulfides, cyclic sulfides, and aliphatic sulfides in a ratio of 3:2:1, respectively (5,6). For high-rank coals, disulfides are not believed to be a significant portion of the total sulfur (5). The amount of thiols is substantially higher in lignites and high-volatile coals than in low-volatile coals (5). The coalification process appears to cause the organic sulfur to change from -SH through R-S-R' to thiophene by cyclization reactions. In summary, the bonding of the organic sulfur with the coal structure varies with the coal rank. The greater rigidity of sulfur present in the higher rank coals renders the sulfur more stable during heat treatment.

The amount of volatile matter evolved during pyrolysis also influences the sulfur evolution process (12). The volatile matter yield of the lower rank coals (hvAb or lower) is significantly higher than that of the higher rank coals. The lower rank coals with higher volatile matter content will retain less sulfur in the residue (by fixation of sulfur by organic or inorganic coal constituents) than the higher rank coals. Finally, the indigenous mineral matter present in coal (particularly calcium and iron compounds) may react and fix sulfur species in the solids during devolatilization.

Transformation of Coal Sulfur During Heat Treatment

The pyrite present in a coal decomposes to ferrous sulfide and sulfur when heated in an inert atmosphere by the following reaction: $\text{FeS}_2 \longrightarrow \text{FeS} + \text{S}$ (Reaction 1, Table 1). This transformation begins at 450 to 500°C and is essentially complete at 850°C. At elevated temperatures, the pyrite may be reduced by carbon (Reaction 3 of Table 1). Examples of reactions of pyrite with hydrogen (donated by coal), CH_4 , or CaSO_4 are shown by the Reactions (4), (5), and (6), respectively (Table 1).

Most aliphatic sulfur compounds decompose appreciably at about 500°C. Diethyl sulfides begin decomposition at ~400°C to form H_2S and mercaptans. Aliphatic and benzylic sulfides, mercaptans, and disulfides lose H_2S between 700 and 800°C. Aromatic sulfides and mercaptans are relatively stable (5) and yield H_2S and CS_2 only at a relatively high temperature (800°C). Examples of the reactions of organic sulfur are summarized in Table 1.

Yergey, et al. (15), performed nonisothermal kinetic studies on sulfur evolution in hydrogen at a relatively slow heating rate (1 to 100°C/min). They developed a kinetic scheme to describe the H_2S evolution in hydrogen. Stinnet, et al. (16), applied the principle of free energy minimization and used the NASA chemical equilibrium code (CEC) to predict the composition of the fixed-bed exit gases, including the sulfur species. In 1932, Snow (13) investigated the conversion of coal sulfur at various peak temperatures in the presence of different gases and reported that first traces of H_2S could be observed at a temperature as low as 200°C. Calkins (10) studied the conversion of coal and model organic sulfur in a rapidly heated fluid-bed reactor.

EXPERIMENTAL


A fixed-bed reactor (slow heating rate organic devolatilization reactor, SHRODR) was used to generate pyrolysis liquids at 500° C. More details on this reactor system and the experimental procedures are available (2,3). A range of feedstocks (primarily coal, but also oil shale, and tar sand) was devolatilized in this reactor. In this study only the coal data were considered. Most coal samples were supplied by


TABLE 1. A Summary of Possible Reactions Involving Sulfur Compounds During Coal Devolatilization

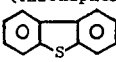
Inorganic

- $\text{FeS}_2 \xrightarrow[500^\circ\text{C}]{\text{inert}} \text{FeS} + \text{S} \longrightarrow \text{Nonvolatile S Compounds}$ (1)
- \downarrow
 $(\text{coal-H}) \longrightarrow \text{H}_2\text{S} + (\text{coal})$ (2)
- $\text{FeS}_2 \xrightarrow[1,000^\circ\text{C}]{(\text{coal C})} \text{CS}_2 + 2 \text{FeS} + (\text{Coal}) \longrightarrow 2 \text{Fe} + \text{CS}_2$ (3)
- $2 \text{FeS}_2 \xrightarrow[230^\circ\text{C}]{\text{H}_2} \text{Fe}_2\text{S}_3 + \text{H}_2\text{S} \xrightarrow[280^\circ\text{C}]{\text{H}_2} 2 \text{FeS} + 5 \text{H}_2\text{S} \xrightarrow[370^\circ\text{C}]{\text{H}_2} 2 \text{Fe} + 2 \text{H}_2\text{S}$ (4)
- Similar Reactions are possible between CO and FeS_2
- $4 \text{FeS}_2 + \text{CH}_4 \xrightarrow[500^\circ\text{C}]{} \text{CS}_2 + 4 \text{FeS} + 2 \text{H}_2\text{S}$ (5)
- $\text{CaSO}_4 + \text{FeS}_2 + \text{H}_2\text{O} \longrightarrow \text{CaO} + \text{FeS} + 2 \text{SO}_2 + \text{H}_2$ (6)

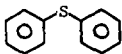
Organic

-  $\xrightarrow[>450^\circ\text{C}]{\text{H}_2} \text{C}=\text{C}-\text{C}=\text{C} + \text{H}_2\text{S} \xrightarrow{\text{H}_2} \text{C}_4\text{H}_{10} + \text{H}_2\text{S}$ (7)
- (Thiophene)

-  $\xrightarrow[500^\circ\text{C}]{\text{H}_2} \text{Thionaphthene} \xrightarrow{\text{H}_2} \text{H}_2\text{S} + \text{C}_6\text{H}_5\text{C}_2\text{H}_5 + \text{C}_6\text{H}_5\text{C}_2\text{H}_7$ (8)
- (Thionaphthene)

-  $\xrightarrow[>550^\circ\text{C}]{\text{H}_2} \text{Dibenzothiophene} + \text{H}_2\text{S}$ (9)
- (Dibenzothiophene)

- $\begin{array}{c} \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ || \quad || \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{HH} \end{array} + \text{H}_2\text{S} \longrightarrow \begin{array}{c} \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ || \quad || \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{S} \end{array} + 2 \text{H}_2$ (sulfur fixation reaction) (10)

-  $\longrightarrow \text{Dibenzothiophene} + \text{H}_2$ (cyclization reaction) (11)
- Diphenyl Sulfide Dibenzothiophene

the Penn State/DOE coal data bank (17). Sample preservation and avoidance of air oxidation of the samples were key considerations in this investigation as reported previously (18-22). Availability of fresh (well-preserved, not weathered) samples was the criterion used for sample selection. Some coal samples utilized by Given, et al. (22), for an investigation on direct liquefaction were selected in this study for comparison with our pyrolysis studies. Primarily bituminous coals were used in this study as these are known to yield the highest liquid product during pyrolysis (1,2). All samples were prepared and handled in an inert atmosphere.

About 25 coal samples, mostly in the high-volatile range, were investigated in this study. The carbon content of the samples ranged between 70 and 80 percent (daf) while the oxygen content ranged from less than 2 to over 20 percent. The sulfur content of these coals varied widely from < 0.5 to over 6 percent (of dry coal). The sulfur type in the feedstocks and the distribution of the sulfur in selected products are provided in Table 2. The Statistical Analysis System (SAS) program developed by the SAS Institute (24) was used for data analysis.

RESULTS AND DISCUSSION

Influence of Coal Type on Sulfur Distribution in Products

A summary of the distribution of coal sulfur to the gaseous, liquid, and solid products resulting during pyrolysis at 500°C is presented by the following equations:

$$\text{Total sulfur in gas} = 0.31 \times S_{\text{coal}} \quad [R^2 = 0.93, F = 425, P = 0.0001] \quad (1)$$

$$\text{Total sulfur in tar} = 0.06 \times S_{\text{coal}} \quad [R^2 = 0.85, F = 175, P = 0.0001] \quad (2)$$

$$\text{Total sulfur in solid} = 0.61 \times S_{\text{coal}} \quad [R^2 = 0.98, F = 1476, P = 0.0001] \quad (3)$$

The above correlations show that for our data set, about 61 percent of the coal sulfur appears in the char while 31 percent of the coal sulfur appears in the gaseous products (sum of H₂S and COS). Only a small portion of the coal sulfur (6 weight percent) evolve as the total sulfur of the pyrolysis liquids. This is partly because a relatively small portion of coal (5 to 25 percent) is converted to liquids during pyrolysis. The water evolved during pyrolysis contains relatively insignificant amounts of dissolved sulfur species.

The R², F- and P-values for the models are also summarized with the equations. R², the coefficient of determination, measures how much of the variation in the dependent variable can be attributed to the model (i.e., independent variable), rather than to random error. R² has been calculated using the regression program of SAS (R² for the no-intercept version was redefined by SAS, Reference 24).

The F-value is the ratio of the mean square for the model divided by the mean square error. It is a test of how well the model as a whole (after adjusting for the mean) accounts for the behavior of the dependent variable. P is the significance value or probability of obtaining at least as great an F value, given that the hypothesis is true. When P < 0.05, the effect is usually termed "significant." For more details on these statistical terms, see Reference 24.

The total gaseous sulfur yield (i.e., sum of H₂S and COS), the major gaseous sulfur products evolved during pyrolysis of coal, can be correlated with the feed dry coal sulfur (Figure 1A). The solid line represents the regression fit through the data. The dotted lines represent 90th percentile confidence limits for the mean predicted values.

TABLE 2. Sulfur Contents of the Coals and the Distribution of the Sulfur in Products (Tar, Char, and Gases)

Coal	Rank	Sulfur Content, Coal				Products			
						(Wt. %, Dry)		(Wt. %, Dry)	
		Total	Pyritic	Organic	Sulfate	Tar	Char	Coal	
						Total	Total	H ₂ S	COS
PSOC 123	hvAb	0.68	0.06	0.61	0.01	0.72	0.45	0.201	0.035
PSOC 181	SubA	0.58	0.04	0.54	0.00	0.54	0.45	0.067	0.025
PSOC 267	hvAb	1.96	0.02	1.89	0.05	0.78	1.00	0.487	0.096
PSOC 275	hvAb	2.14	1.41	0.73	0.00	1.17	2.46	0.503	0.098
PSOC 296	hvAb	0.98	0.91	0.07	0.00	0.73	0.91	0.436	0.034
PSOC 306	hvAb	2.05	1.21	0.83	0.01	1.54	1.72	0.559	0.083
PSOC 355	hvAb	2.77	2.12	0.63	0.02	1.02	2.27	0.605	0.177
PSOC 375	hvAb	1.11	0.38	0.68	0.05	0.90	1.20	0.415	0.060
PSOC 1109	hvCb	1.82	0.78	0.71	0.33	0.75	2.02	0.348	0.073
PSOC 1313	mvb	5.65	4.52	0.98	0.51	2.57	4.23	1.040	0.231
PSOC 1323	hvBb	4.10	1.47	2.29	0.34	2.39	3.10	1.491	0.216
PSOC 1448	hvAb	0.46	0.04	0.41	0.01	0.22	0.36	0.190	0.028
PSOC 1449	hvAb	1.64	0.53	1.09	0.02	0.55	2.08	0.560	0.103
PSOC 1469	hvAb	0.79	0.26	0.51	0.02	0.46	0.56	0.236	0.051
PSOC 1470	hvAb	2.50	1.88	0.58	0.04	--	--	--	--
PSOC 1471	hvAb	1.04	0.22	0.79	0.03	0.55	0.73	0.468	0.074
PSOC 1472	hvAb	0.85	0.28	0.55	0.02	0.38	0.62	0.406	0.031
PSOC 1473	hvAb	0.63	0.08	0.53	0.02	0.30	0.49	0.207	0.025
PSOC 1475	hvAb	0.98	0.32	0.64	0.02	0.41	0.67	0.300	0.049
PSOC 1481	hvAb	4.82	3.20	1.42	0.20	2.10	3.88	1.061	0.248
PSOC 1492	hvCb	4.35	1.82	2.50	0.03	2.24	3.20	1.325	0.222
PSOC 1499	hvAb	0.67	0.02	0.65	0.00	0.34	0.53	0.278	0.061
PSOC 1502	hvCb	0.51	0.15	0.36	0.00	0.25	0.40	0.229	0.051
PSOC 1504	hvAb	0.77	0.04	1.21	0.02	0.41	0.54	0.284	0.088
PSOC 1517	hvAb	1.92	0.70	1.21	0.01	0.41	1.89	0.779	0.131
PSOC 1520	SubC	1.21	0.05	1.15	0.01	0.50	1.08	0.401	0.043
PSOC 1523	hvAb	0.71	0.02	0.69	0.00	0.53	0.48	0.373	0.054
PSOC 1524	hvAb	1.85	1.39	0.44	0.02	0.81	1.81	0.571	0.046
PITT No. 8	hvAb	1.99	0.34	1.08	0.13	0.72	1.77	0.359	0.067
OHIO No. 6	hvCb	2.91	--**	--	--	0.88	2.46	0.462	0.229
WELLMORE No. 8	hvAb	1.23	--	--	--	0.43	0.95	0.507	0.051
AMAX*	hvAb	0.91	--	--	--	0.35	0.58	0.316	0.038

* Physically/chemically cleaned by AMAX process. Kentucky Hazard coal.

** Not available.

A single, variable model (total coal sulfur) was used to predict the sulfur yield. The predicted and experimental H_2S and COS are compared in Figures 1B and 1C. The following equations describe the yields of these gaseous species:

$$[H_2S] = S_{\text{coal}} \times 0.259 \quad [R^2 = 0.91, F = 319, P = 0.0001] \quad (4)$$

$$[COS] = S_{\text{coal}} \times 0.050 \quad [R^2 = 0.94, F = 504, P = 0.0001] \quad (5)$$

In these equations $[H_2S]$ and $[COS]$ signify weight percent of coal sulfur as H_2S and COS in the products. The combined amount represented by Equations 4 and 5 agrees with the amount represented by Equation 1. Additional two-variable models (including the total sulfur and organic sulfur) facilitated improved predictions of the experimental results. These results will be discussed in a separate communication.

The sulfur content of the pyrolysis tar (weight percent) can be predicted based on the coal sulfur (weight percent dry coal) as shown in Figure 2A. The following equation describes this prediction:

$$S_{\text{tar}} = 0.467 \times S_{\text{coal}} \quad [R^2 = 0.946, F = 522, P = 0.0001], \quad (6)$$

where S_{tar} equals weight percent sulfur in tar, and S_{coal} equals weight percent sulfur in dry coal.

The finding shows that the pyrolysis liquids contain less than half as much sulfur as the parent coal (for the same amount of fuel by weight).

The correlations between the pyritic, organic, or sulphatic sulfur in the coal and the sulfur content of the tar were poor.

The char sulfur (weight percent char) can be correlated with the sulfur content of the parent coal (weight percent dry coal), as shown in Figure 3A. The total char sulfur content (weight percent of char) can be correlated somewhat with the pyritic sulfur content of the parent coal (Figure 3B). The greater the pyritic sulfur content of the coal, the larger the char sulfur. From a thermodynamic standpoint, pyrite is unstable above 450°C . Not all pyrite is decomposed at 500°C even when a long residence time (~ 40 min) is maintained at a temperature above the pyrite decomposition temperature. This finding suggests that the kinetics of pyrite decomposition and reaction strongly influences the amount of sulfur liberation. The sulfur content of the char can be predicted based on the feed coal sulfur (dry basis). The following equation represents this relationship:

$$S_{\text{char}} = S_{\text{coal}} \times 0.81 \quad [R^2 = 0.975, F = 1192, P = 0.0001], \quad (7)$$

where S_{char} = sulfur content of char (weight percent), and S_{coal} = sulfur content of coal (weight percent).

Influence of Peak Pyrolysis Temperature on Sulfur Distribution in Products

To investigate the influence of the peak devolatilization temperature on sulfur evolution during coal pyrolysis, Pittsburgh No. 8 coal was pyrolyzed to various peak temperatures. Data on the influence of the peak pyrolysis temperature on product distribution and quality have been reported (2,3). This coal contained about 2 weight percent sulfur (dry basis). The correlation coefficient between the total gaseous sulfur content (summation of COS and H_2S , expressed as the weight percent of dry feed coal sulfur) with the pyrolysis temperature (between 400 and 725°C) was 0.99 (Figure 4). The general regression model [GLM] of SAS provided the following relationship on sulfur yield for the temperature range 400 to 725°C :

$$\text{Total S in gas} = (0.00103) \times (\text{Temp, in}^\circ\text{C}) \quad [R^2 = 0.99, F = 234, P = 0.0006] \quad (8)$$

An increase in temperature resulted in an increase in the sulfur content of the tar (expressed as weight percent of the feed dry coal sulfur). As one would expect, the total and pyritic sulfur content of the char decreased as the peak heat treatment temperature increased. In contrast, the char organic sulfur content increased (data not shown) with an increase in the heat treatment temperature. The influence of peak pyrolysis temperature or heating rate on the sulfur distribution in products for additional coals will be addressed in future studies.

SUMMARY AND CONCLUSIONS

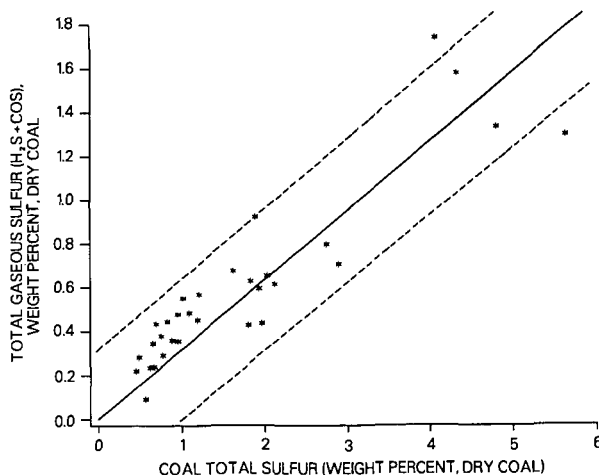
The results of this study demonstrate that the total gaseous sulfur ($H_2S + COS$) generated during coal pyrolysis can be correlated with the total coal sulfur. Furthermore, total coal sulfur could be utilized to predict the yields of H_2S or COS species individually. Correlations between the feed coal sulfur and char or tar sulfur have been obtained. The char sulfur could be correlated somewhat with the pyritic sulfur content. However, correlations between sulfur type (organic, pyritic, or sulfatic sulfur) with sulfur content in the products were generally poor. Multivariate analysis will be performed in the future to understand the role of sulfur type (e.g., pyritic, organic, or sulfatic sulfur) on their distribution.

The essence of this investigation is the development of a number of correlations for relating the distribution of coal sulfur into solid, liquid, or gaseous products occurring during pyrolysis. It is shown that about 61 percent of coal sulfur appears in the char while about 31 percent of coal sulfur appears as gaseous products when coal is pyrolyzed at a relatively low temperature ($500^\circ C$). With an increase in the peak devolatilization temperature, however, the gaseous sulfur yield increases monotonically for the Pittsburgh No. 8 coal at the expense of char sulfur.

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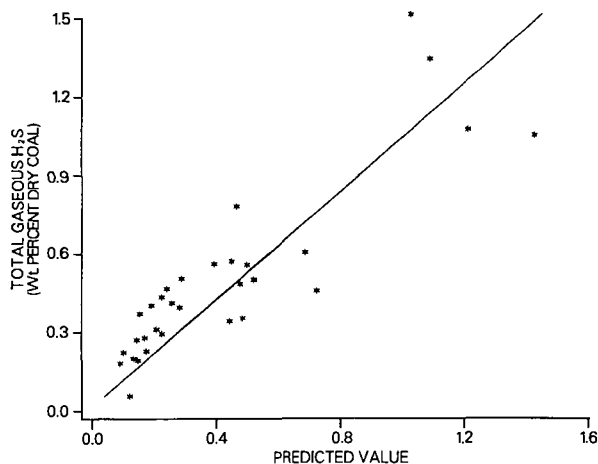
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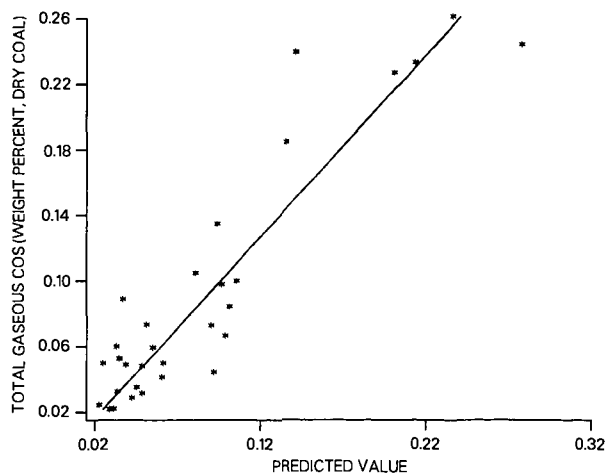
Figure 1A. The relationship between the total gaseous sulfur with the feedstock sulfur content (weight percent, dry coal). The solid line represents the regression through data. The dashed lines represent 90th percentile confidence limits for the mean predicted values.

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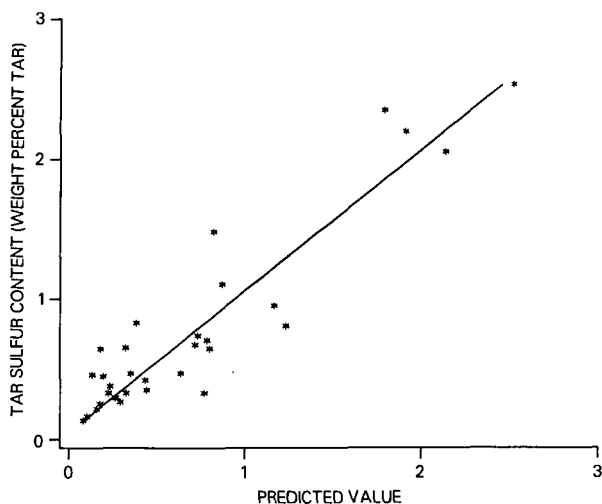
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Figure 1B. A comparison between the predicted and actual H_2S yield. The prediction was based solely on the sulfur content of the coal (weight percent, dry coal).



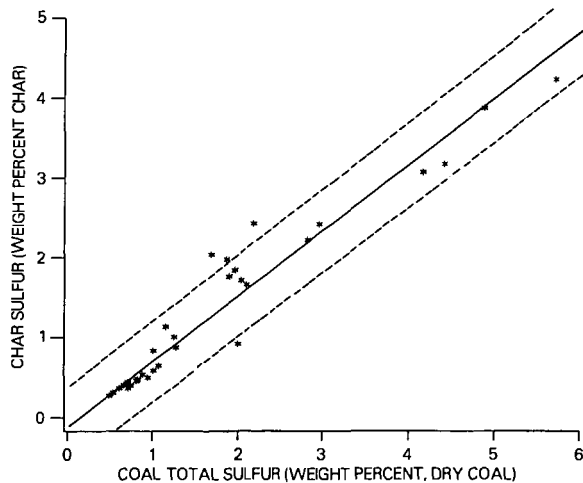
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Figure 1C. A comparison between the predicted and actual COS yield. The predictions were based on feed sulfur content (weight percent, dry coal).



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Figure 2. A comparison between the predicted and measured sulfur content of the pyrolysis tar (weight percent of tar). The prediction was based on coal sulfur (weight percent dry coal).



188-800-3A BP4

Figure 3A. The comparison between the char sulfur content (weight percent char) with the feed coal sulfur content (weight percent, dry coal). The solid line represents the regression through the data. The dashed lines represent 90th percentile confidence limits for the mean predicted values.

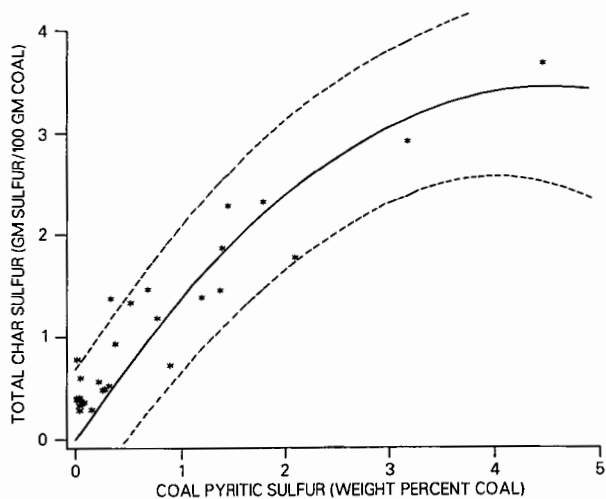


Figure 3B. A relationship between the char sulfur content (weight percent char) with the pyritic sulfur content (weight percent, dry coal). The solid represents the regression through the data. The dashed lines represent 90th percentile confidence limits for the mean predicted values.

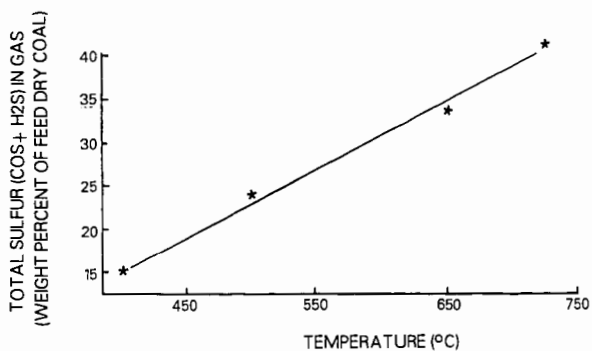
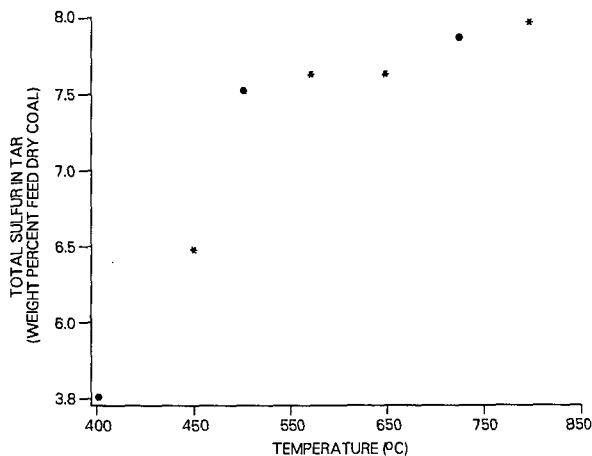
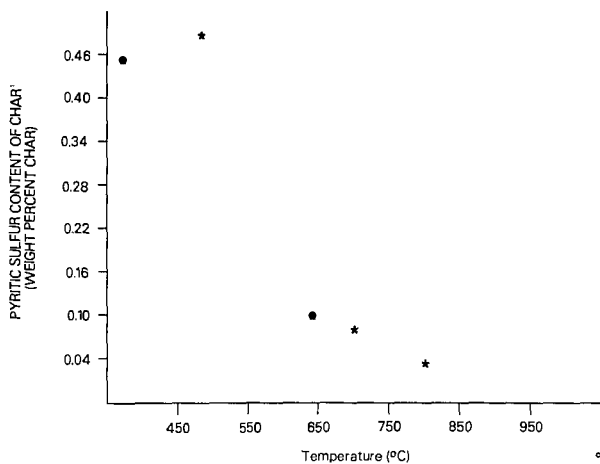


Figure 4. Influence of peak pyrolysis temperature on total gaseous sulfur yield ($H_2S + COS$) as a function of temperature.



C68-900-Z BP4

Figure 5. Influence of peak pyrolysis temperature on tar sulfur content (weight percent of tar).



C68-09A-A BP1

Figure 6. Pyritic sulfur content in char prepared at various peak temperatures.

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Distribution of Sulfur During Coal Pyrolysis in a High Pressure Entrained-Flow Reactor

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Introduction

An understanding of the fundamental and interrelated processes involved in coal pyrolysis/gasification is essential in order to advance gasification technologies. Therefore, it is necessary to generate data on the effect of coal properties and operating conditions on coal devolatilization behavior under conditions similar to those in advanced-concept gasifiers; typically, a high-temperature and high pressure environment for entrained coal particles.

The thermal decomposition of raw coal produces solid char/coke plus some liquid (tar) and gaseous products.⁽¹⁾ Tars are vapors at the pyrolysis temperature, but are usually heavy liquids or solids at room temperature. The chars, which usually account for between 30-70% of the original coal, consist mainly of carbon, along with small amounts of H, O, N and S as well as the ash which results from the mineral matter. The quantity and quality of the char, tar and gases produced during pyrolysis depend on the chemical and physical properties of the coal (i.e. coal type, particle size, etc.) as well as on the pyrolysis conditions (i.e. temperature, pressure, etc.).⁽¹⁾

Due to the environmental impact of the emission of SO₂ during combustion, pre-combustion processing may be necessary to reduce the sulfur content of so-called "high sulfur coals". Desulfurization of coal prior to combustion can be achieved by one or more of the following methods.⁽²⁻⁴⁾ 1) Advanced physical cleaning -- this method involves a variety of approaches (i.e. froth flotation, float-sink, etc.) for reduction of pyrite in the coal based on the differences between the density of pyrite (5.0 g/cm³) or marcasite (4.87 g/cm³)⁽⁵⁾ and the organic matrix (1.2-1.5 g/cm³).⁽⁶⁾ 2) Chemical coal cleaning -- based on the concept of breaking the chemical bonds of the organic sulfur by exposing the coal usually to molten chemicals such as sodium hydroxide. 3) Conversion of the coal to low-sulfur liquid and gaseous fuels -- based on liquefaction and gasification technologies.

According to the literature, there are three commonly recognizable forms of sulfur in coal: sulfate, pyrite and organic sulfur. Although the distribution of various forms of sulfur is less often determined than the total sulfur, their presence can have a significant effect on coal utilization. However, the degree to which the sulfur can be reduced and/or removed from the coal by the above techniques is strongly dependent on the forms of sulfur present in the coal. Therefore, accurate analytical data on the forms of sulfur is a requirement for improving removal processes.

Pyrolysis has been used by some researchers to study the behavior and distribution of sulfur in coal.⁽⁷⁻¹²⁾ Some investigators have also used pyrolysis in order to study the chemistry and kinetics of reactions involving sulfur-containing compounds in coal.⁽¹³⁻¹⁵⁾ The purpose of the current work was to determine the distribution of the total sulfur between the products of pyrolysis (tars and chars) and the various forms of sulfur in the chars from pyrolysis of a subbituminous coal in a high pressure entrained-flow reactor.

Experimental

A schematic diagram of the entrained-flow reactor used in this study is shown in Figure 1. This reactor is capable of subjecting pulverized coal particles to temperatures and pressures as severe as 1373 K and 1000 psig, respectively. It is also equipped with a computerized data

acquisition system for rapid data collection and monitoring of the experimental conditions. The operating principle and procedure have been described elsewhere.^(16,17)

Pyrolysis experiments were performed on pulverized and sized samples, $\sim 57 \mu\text{m}$ mean diameter, of Montana Rosebud Subbituminous coal at 1189 K, 100-900 psig applied N_2 pressure and 0.1-1.7s residence time. The collectable products of pyrolysis, both solid and the material trapped on the filter, were extracted in conventional Soxhlet apparatus using tetrahydrofuran (THF) as the solvent. The extracted material represented the tars from pyrolysis while the THF insoluble material represented the char. The gaseous products from pyrolysis were analyzed qualitatively and quantitatively at steady-state operation by an on-line Carle gas chromatograph capable of monitoring the following gases: H_2 , N_2 , O_2 , H_2S , CO , CO_2 , CH_2 , C_2H_4 , C_2H_6 , H_2O , SO_2 , and C_3+C_4 hydrocarbons. An infrared gas analyzer was used to continuously monitor the CO concentration in the outlet gas stream. This was needed to determine when steady state operation had been reached.

Proximate analyses were performed on the raw coal and the chars using a Leco MAC-400 analyzer. Ultimate analyses were also performed on raw coal, chars and tars using a Leco CHN-600 analyzer. Total sulfur contents of the raw coal, tars and chars were determined by a Leco SC-132 sulfur analyzer. Sulfate and pyritic sulfur in the raw coal and the chars were determined according to the American Society for Testing and Materials (ASTM) standard procedure D-2492.⁽¹⁸⁾ Organic sulfur for the raw coal and chars was calculated by subtracting the percentage sums of sulfate and pyritic sulfur from the total sulfur. Higher heating values were measured for both the raw coal and the chars using a Parr model 1241 adiabatic bomb calorimeter. Full analyses of the Montana Rosebud coal are shown in Table 1.

Coal particle residence times in the furnace were determined using a computer flow model. The governing equations have been discussed elsewhere.^(16,17) Weight loss due to the coal devolatilization was calculated by using ash as a tracer. Tar yields (~ 5 -15%) were measured from the total amount of THF solubles collected and expressed as weight percent of coal (daf) fed into the reactor. Total gas yields were calculated from the difference between the weight loss and tar yield.

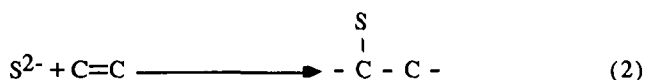
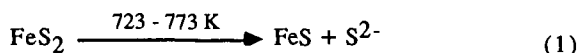
Results and Discussion

Pyrolysis results on weight loss, tar and gas yields and gaseous compositions have been reported and discussed in detail elsewhere.^(16,19,20) Total and forms of sulfur (daf) for the raw coal and selected chars from pyrolysis of Montana Rosebud coal at 1189 K, 100-900 psig applied N_2 pressure and 0.3-1.7s residence time are shown in Table 2. Total sulfur analyses of the corresponding tars are also shown in Table 2.

A comparison of the total sulfur (daf) contents of the chars and tars (Table 2) clearly indicates that the sulfur in the chars is always higher than the sulfur in the tars produced from the pyrolysis experiments. In most cases the sulfur content of the tars was about 50% lower than the sulfur content of the corresponding char and the raw coal. It was observed that as the residence time of pyrolysis increased, the sulfur content of the tar increased, as shown in Figure 2.

The reason for the increase in the sulfur content of the tar with increasing pyrolysis residence time might be the higher rate of decomposition of pyrite in the coal and the secondary reactions between the decomposition product and the tar molecules in the gas phase. This is supported by the data in Figure 3. As can be seen, the pyritic sulfur content of the chars decreases as the pyrolysis residence time increases.

It has been shown by Given et al.⁽²¹⁾ and others that pyrites decompose between 724-773 K. The produced ferrous sulfide and free sulfur (S^{2-}) then react with the organic matrix of the tars and chars by crosslinking according to the following reactions.^(14,22)



The effect of pressure on the pyritic sulfur content of the chars produced from pyrolysis of Montana Rosebud subbituminous coal is shown in Figure 4. As the pressure increases, the pyritic sulfur content of the chars increases. This indicates that increasing the pyrolysis pressure reduces the rate of the pyrite decomposition reactions.

Reductions in the total sulfur content of the coal were calculated according to the following equation:^(10,12)

$$\% S_t = \left\{ (S_t)_{\text{Raw Coal}} - [(S_t)_{\text{Char}} \times (\text{char yield})] / (S_t)_{\text{Raw Coal}} \right\} \times 100$$

The effect of residence time on the percent reduction in total sulfur is shown in Figure 5. As the pyrolysis residence time increases, the percent reduction in sulfur content of the coal increases, meaning a higher reduction in total sulfur can be achieved by increasing the pyrolysis residence time. This is supported by the data in Figure 2. The decrease in pyritic sulfur with increasing residence time is most likely the reason behind the increase in the percent reduction in the total sulfur content with increasing pyrolysis residence time.

The effect of pressure on the percent reduction in the total sulfur content of the coal is shown in Figure 6. It was observed that as the pyrolysis pressure increased, the percent reduction in the total sulfur content decreased. In other words, increasing the pyrolysis pressure reduces the percent total sulfur reduction. This behavior is probably due to the fact that increasing the pyrolysis pressure reduces the decomposition of pyrite, Figure 4, which in turn affects the overall percent reduction in the sulfur content of the chars.

It has been reported that H_2S is the dominant sulfur-containing species produced by high-temperature ($>1073 \text{ K}$) pyrolysis.^(14,15,22) H_2S is the result of desulfurization reactions between the H_2 , generated by the decomposition of the coal matrix during pyrolysis, and pyrites according to the following equations:



However, some of the produced H_2S reacts with the tars and chars as soon as they are formed and becomes organically bonded to the products. This is due to the availability of active carbon sites in the chars produced during devolatilization of the coal matrix, and in the reactive organic species formed during secondary cracking reactions of the tars. This is supported by the fact that the secondary cracking reactions of the tars increase as the pyrolysis residence time increases, and the data in Figure 2, which indicate that as the pyrolysis residence time increases the total sulfur in the tars increases.

Conclusions

Based on the information available in the literature and the data presented here on the pyrolysis of Montana Rosebud subbituminous coal the following can be concluded:

- 1) Total sulfur in the tars produced during pyrolysis is residence time dependent.
- 2) Forms of sulfur in the chars produced from pyrolysis revealed that pyritic sulfur is most affected by the pyrolysis conditions (residence time and pressure).
- 3) A higher percent reduction in total sulfur can be achieved by increasing the pyrolysis residence time.
- 4) Increasing the pyrolysis pressure reduces the percent total sulfur reduction.
- 5) The dominant species from the decomposition of pyrite in the coal at high-temperatures is H_2S . However, some of the evolved H_2S reacts with the chars and tars, especially at higher residence times.

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Table 1.

Characteristics of Montana Rosebud Subbituminous Coal

<u>Proximate Analysis</u>	<u>(wt%, dry)</u>
Moisture	--
Ash	10.31
Volatile Matter	36.50
Fixed Carbon	53.19
 <u>Ultimate Analysis</u>	
Ash	--
Carbon	83.89
Hydrogen	3.72
Nitrogen	1.38
Total Sulfur	1.12
Oxygen (by diff.)	9.89
 <u>Forms of sulfur</u>	
Pyritic	0.217
Sulfatic	0.092
Organic	0.814
Total	1.123
 Heating Value (Btu/lb, daf)	 13929

Table 2.

Sulfur Analyses of the Tars and Chars From Pyrolysis of Montana Rosebud Subbituminous Coal at 1189 K, 100-900 psig N₂ Pressure and 0.3-1.7s Residence Times.

Sample(a)	Total Sulfur (wt%, daf)		Forms of Sulfur (wt%, daf)		
	Tar	Char	Pyritic	Sulfatic	Organic(b)
Raw Coal	--	--	0.217	0.092	0.814
100-0.3	0.54	0.92	0.209	0.101	0.608
100-1.0	0.82	1.16	0.098	0.079	0.983
100-1.7	0.97	0.88	0.044	0.073	0.766
178-0.3	0.75	1.17	0.220	0.132	0.822
178-1.0	0.70	0.89	0.121	0.154	0.608
178-1.7	0.97	0.99	0.008	0.076	0.902
309-0.3	0.51	1.01	0.144	0.119	0.748
309-1.0	0.90	0.96	0.125	0.120	0.709
309-1.7	1.02	1.18	0.021	0.166	0.989
530-0.3	0.40	0.84	0.272	0.151	0.520
530-1.0	0.68	1.17	0.190	0.142	0.833
900-1.0	0.62	1.42	0.304	0.162	0.954

(a) Pressure-Residence Time

(b) By Difference

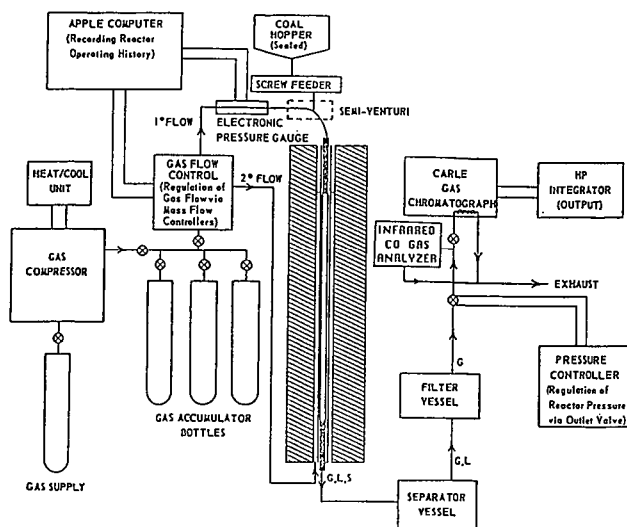


Figure 1. Configuration of High Pressure Entrained-Flow Reactor

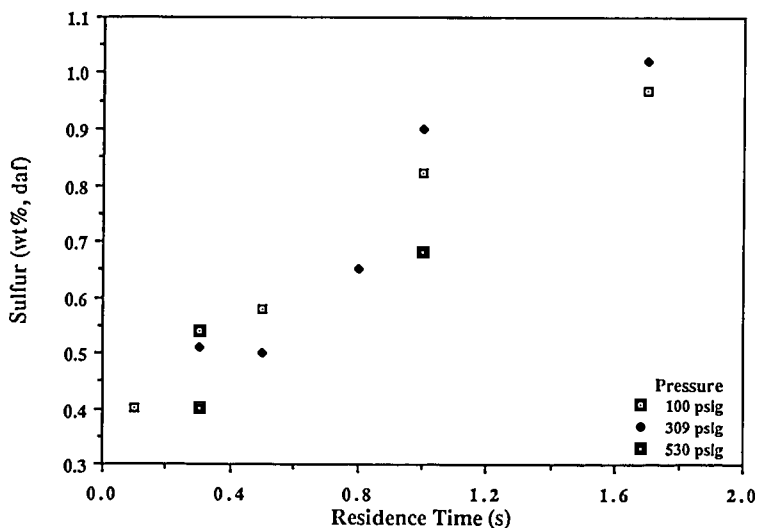


Figure 2. Effect of Residence Time on Total Sulfur (daf) of Tars from Pyrolysis of Montana Rosebud Coal at 1189 K

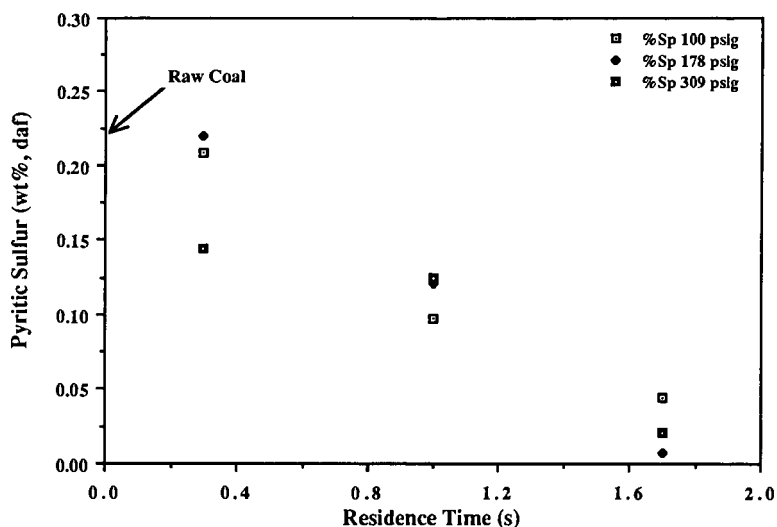


Figure 3. Effect of Residence Time on Pyritic Sulfure of the Chars from Pyrolysis of Montana Rosebud Coal at 1189 K

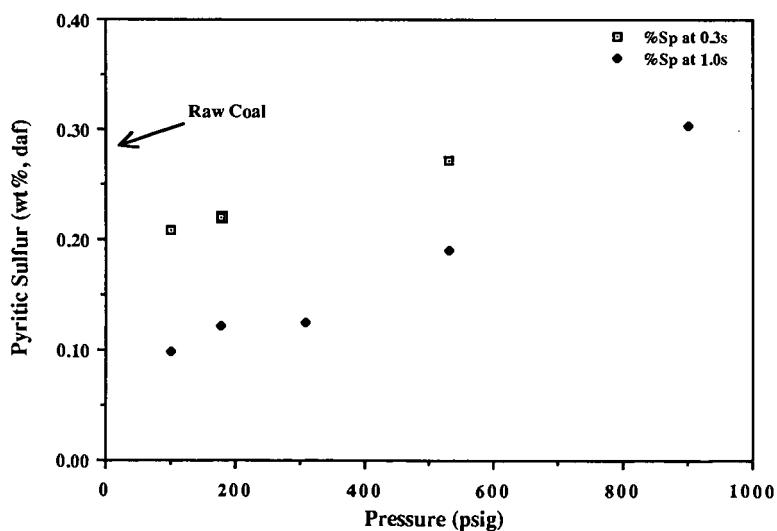


Figure 4. Effect of Pressure on Pyritic Sulfur of the Chars from Pyrolysis of Montana Rosebud Coal at 1189 K

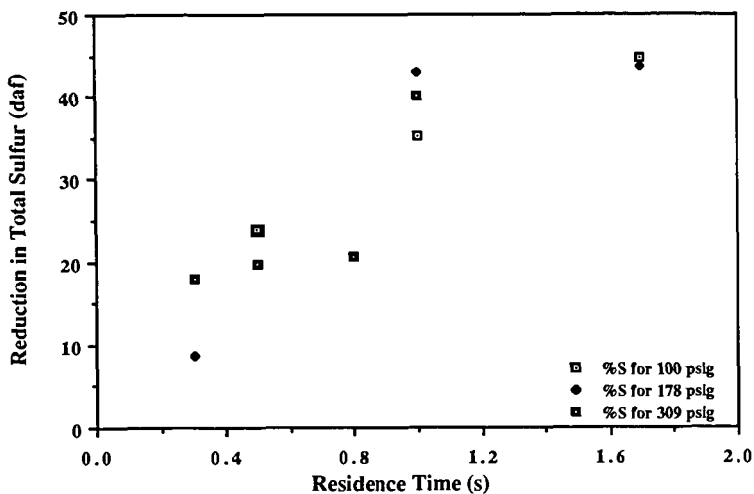


Figure 5. Effect of Residence Time on Percent Reduction in the Total Sulfur of Montana Rosebud Coal Pyrolyzed at 1189 K

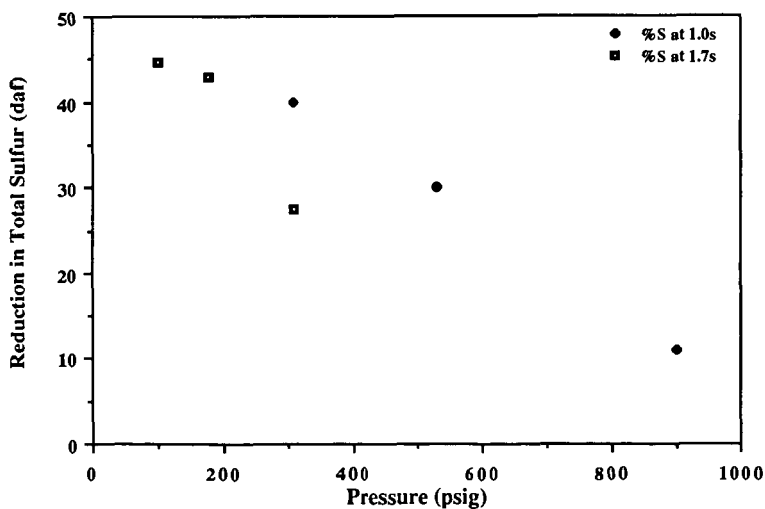


Figure 6. Effect of Pressure on Percent Reduction in the Total Sulfur of Montana Rosebud Coal Pyrolyzed at 1189 K

EVOLUTION OF SULFUR GASES DURING COAL PYROLYSIS

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1. Introduction

The yields and rates of evolution of sulfur gases depend not only on pyrolysis conditions but also on the coal itself (1). The organic/inorganic forms of sulfur, as well as the secondary reactions of sulfur gases with solids and with other pyrolysis-generated gases, play an important role. Monitoring the time- and temperature-dependent evolution of sulfur-containing gases provides insight into the sulfur chemistry affecting evolution profiles (1,2). Programmed-temperature studies of sulfur gas evolution often have been limited to H_2S . In some cases, all sulfur gases have been studied collectively by reducing or oxidizing them to H_2S or SO_2 (3,4). Recently, Calkins (5) studied the evolution of individual sulfur species from a Pyroprobe using Gas Chromatograph/Mass Spectrometer (GC/MS) and from isothermal flash pyrolysis. Boudou et al. (6) also identified some individual sulfur gases from isothermal pyrolysis using a Curie-point reactor in combination with MS, GC, and GC/MS.

In this study, we monitored the real-time evolution of sulfur gases during slow-heating pyrolysis via a triple quadrupole mass spectrometer (TQMS). We also monitored the evolution of hydrocarbon gases, water, and carbon oxides. We compared the evolution profiles of sulfur gases and related them to the rank of the coal, the organic and inorganic sources of sulfur in each coal sample, and the evolution of other pyrolysis-generated gases. We also studied the extent of secondary reactions by varying the pyrolysis conditions.

2. Experimental

A schematic of the experimental set-up is shown in Fig. 1. Coal was pyrolyzed in a 1.5-cm-i.d. quartz tube, placed in a 1.9-cm-i.d. three-zone furnace. The control thermocouples for the top and bottom zones were embedded in the furnace wall, while the thermocouple for the mid-zone was placed between the furnace wall and the reactor. Another thermocouple was inserted into the center of the coal-sand bed, and the average bed temperature was calculated from the wall and the center temperatures. Coal particles were diluted with quartz sand to prevent the bed from being plugged because of softening and agglomeration of coal. Coal was then heated from 25°C to 900°C at a heating rate of 4.5°C/min.

To examine the effect of secondary reactions on the observed products, we varied the amount of coal from 0.5 to 2.5 g and the argon flow rate from 34 to 169 cc/min. Compared to our reference conditions of 0.5 g and 34 cc/min, the experiment with sample size of 2.5 g and 34 cc/min argon flow represents a five-fold increase in pyrolysis gas partial pressure at nearly constant gaseous residence time. For the experiment in which both the sample size and argon flow were increased, gaseous partial pressures remained constant, but the gaseous residence time decreased.

To monitor the evolution of water and naphtha, including thiophenes, we heated all the parts, from the pyrolyzer to the TQMS. A constant flow of argon swept volatiles to a glass wool trap that was placed in an oven at -130°C to condense high boiling liquid products (tar). All transport lines from the trap to the TQMS were maintained at $T > 140^\circ\text{C}$.

In the TQMS operation, both normal mass scans (ms mode) and daughter ion scans (ms/ms mode) were used in all experiments. Details of the TQMS and the ms and ms/ms mode operation were described elsewhere (7). Table 1 summarizes the parent/daughter pairs for sulfur gases we monitored. All gases in Table 1, except H_2S and SO_2 , are calibrated using analyzed commercial standards with the concentration levels about 200 ppm. We used a 981-ppm standard for H_2S , and SO_2 was not calibrated.

We chose eight Argonne premium coal samples for our work because of their diverse properties, high quality, and wide-spread use by other researchers. Among the eight coals, we studied in detail two coals with the highest and the lowest sulfur contents. Illinois No. 6 high volatile bituminous coal (ILHVB) had the highest sulfur content (5.4%), while Blind Canyon Seam high volatile bituminous coal (BCHVB) had the lowest (0.5%). The properties of these two coals, provided by Argonne National Laboratory or obtained from literature (8), are shown in Table 2. Samples were stored under nitrogen and we saw no aging effects. Sulfur gases from other coals are discussed qualitatively based on the data obtained from pyrolysis in a stainless steel reactor. In those experiments with the stainless-steel reactor, the main goal was to study hydrocarbon gases under well-defined temperatures.

3. Results

The TQMS has the sensitivity, selectivity, and speed to monitor the real-time evolution of individual species in a complex pyrolysis gas mixture. We monitored H_2S and CH_3SH in both ms and ms/ms modes, while other sulfur gases were monitored only in ms/ms mode which was necessary to differentiate them from hydrocarbon gases of the same molecular mass. For H_2S and CH_3SH , $m/z = 34$ and 48 in ms mode are free of hydrocarbon interferences because $m/z = 34$ and 48 are rare fragments of hydrocarbons. However, $m/z = 48$ has to be corrected for SO_2 fragments when SO_2 is abundant.

For all eight coals, there are three temperature regions at which sulfur gases evolve under the given time-temperature history. Although the exact temperature of the maximum rate of evolution (T_{max}) varies with the coal, the three regions are roughly $< 200^\circ\text{C}$, 400°C - 500°C , and 500°C - 600°C .

At temperatures lower than 200°C , the only sulfur gas observed was SO_2 . Low temperature evolution implies the existence of loosely bound, trapped, or adsorbed SO_2 . However, SO_2 evolution seems to be very sensitive to pyrolysis conditions. More low-temperature SO_2 was detected as the ratio of coal to sweep-gas flow rate was increased. Experiments with a 316-stainless-steel reactor showed no SO_2 at this temperature region, suggesting a reaction of SO_2 with the stainless steel.

Figure 2 shows evolution profiles of eight other sulfur gases between 200 and 800°C from two coals, ILHVB (solid lines) and BCHVB (dotted lines). Because of the low sulfur content of BCHVB, only four major sulfur gases were detected. Most of the organic pyrolysis reactions occur between 350 and 500°C . While all gases have a peak in this temperature region, H_2S , COS , and CS_2 have a second peak between 550 and 600°C . While the high temperature source is clearly pyrite decomposition, the lower temperature source is more complicated.

Figure 3 compares the evolution profile of four organic sulfur compounds with the corresponding hydrocarbons. The sulfur compound precedes its corresponding hydrocarbon in all cases. While T_{max} for CH_4 is substantially higher than those for other hydrocarbons, methanethiol is evolved at approximately the same temperature as the other thiols.

The evolution profiles in Fig. 2 are similar to those reported previously for Green River shale. Burnham et al. (2) noted that most of the H_2S evolved in the 550°C region could be shifted to the 400 - 450°C range if pyrolysis occurs under self-

purging conditions (no auxiliary gas sweep). To explore this effect and other secondary reactions, we conducted two additional experiments on ILHVB coal. Table 3 compares the amounts of sulfur gases evolved under our standard conditions to those evolved from experiments representing higher product partial pressure (P_{vol}) at similar residence time and shorter gaseous residence time (t_{res}). The amounts of H_2S formed in the two temperature regions show no clear changes with these variations in conditions. The only observable effects are increased COS generation in the 550°C range at shorter t_{res} and changes in the amounts of CS_2 .

In Fig. 4, we report T_{max} for H_2S and hydrocarbons from the experiments with a stainless-steel reactor. Even though some aspects of the sulfur-gas profiles were affected by reactions with the steel, Fig. 4 shows that T_{max} for H_2S depends on coal rank. The increase in T_{max} of the low temperature peak with the rank is greater than a similar increase in T_{max} for total organic volatiles (total ion current minus Ar, CO_2 , CO, H_2O , and H_2S). T_{max} for the high temperature H_2S peak shows more scatter, so the trend is not as clearly present as the low temperature H_2S peak. However, Whelen et al. (9) also observed an increase in T_{max} of both COS peaks with maturity in Type III kerogens, which suggests that our high temperature trend is real.

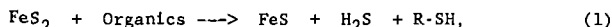
4. Discussion

An obvious goal is to be able to relate the amounts and kinds of various sulfur components to the sulfur composition of the original coal and the processing conditions. The results in this paper provide only a small fraction of the information needed to achieve that goal. However, we have made significant progress.

The sulfur evolution profiles at temperatures between 400 and 500°C are a poorly defined combination of organic pyrolysis reactions and pyrite reactions. The source of sulfur can be both sulfur in the organic matrix as well as pyritic sulfur. Coal-matrix sulfur, especially in high volatile bituminous coals, exists as sulfides and thiophenes (4,5). Thus, sulfides and thiophenes are probably primary products of pyrolysis or products of tar cracking. Thiophenes are very stable at $T < 500^\circ C$, so they are not likely to go through gas phase secondary reactions. Hydrocarbon gases such as acetylene are also known to react with pyrite to form thiophenes (1). However, we found that, for Green River shale, removal of pyrite by acid treatment (7) and doping low-sulfur shales with pyrite (10) had negligible effects on the amount of thiophenes generated.

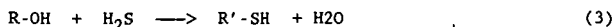
In contrast, H_2S and thiols can be generated by pyrite reactions. Pyrite decomposition is a strong function of grain size, gas environments, and pyrolysis conditions (2,11). Although the H_2S evolved below 500°C from well-swept fine particles can be attributed to organic sulfur (7), it can be shown from other data (2,7,12) that about two-thirds of the H_2S evolved below 500°C from Green River shale under self-purging conditions comes from pyrite. Unfortunately, we did not see any clear effect of pyrolysis conditions on H_2S formation reactions in ILHVB, as shown in Table 3. Apparently our range of conditions was too small to see the marked differences between gas sweep and self-purging conditions observed previously for Green River shale (2,13). We are also investigating other explanations for our observation, such as the effect of pyrite grain size and crystal structure.

Attar (1) indicated that organic matter can react with pyrite at temperatures as low as 250°C. The important reactions can be summarized in Reaction 1.



As implied in Reaction 1, the major source of hydrogen in H_2S formation reaction at these temperatures is probably hydrocarbons and hydrocarbon radicals both in

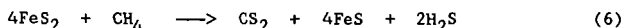
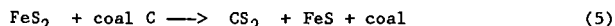
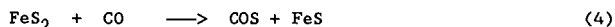
condensed and gas phases. H_2S and thiols are also likely to be involved in secondary reactions. For example,



For thiols, the gas phase secondary reactions may dominate, because the rate of evolution maximizes when H_2S evolution maximizes.

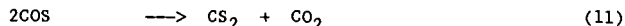
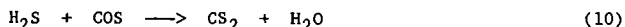
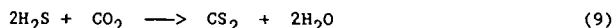
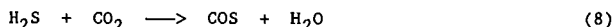
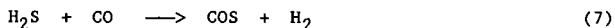
The results in Figure 2 show that only a few of the sulfur-containing compounds (H_2S , COS and CS_2) are related to high-temperature pyrite reactions. Near 600°C , the evolution of hydrocarbon gases from pyrolysis, except CH_4 , is essentially completed. Other pyrolysis gases available at this temperature are CO, CO_2 , H_2O , and H_2 , of which the amounts are affected by char gasification, mineral dehydration, water-gas shift reaction, and carbonate mineral decomposition where possible. For the coal with high pyritic sulfur such as ILHVB, sulfur gases at this temperature are mainly from pyrite decomposition. Pyrite decomposes rapidly at temperatures above 550°C , and H_2S is the major product of pyrite decomposition. In our experiments, the source of hydrogen is probably H_2 , H_2O , and hydrogen in char; but the relative importance of each hydrogen donor is not yet clear.

Reactions to form COS and CS_2 can be both gas-solid and gas phase secondary reactions. The pyrite reactions are:



In his review, Attar (1) claimed Reactions 4 and 5 are slow at $T < 800^\circ\text{C}$. However, Taylor et al. (14) found that the rate of formation of COS from the reaction of pyrite and 1% CO in argon was significantly fast even at 500°C . Calkins (5) suggested Reaction 6 takes places at $T > 800^\circ\text{C}$, so it may also be slow at the temperatures of interest here.

Examples (15) of the possible gas phase reactions at this temperature are:



Reaction 10 is known to occur at temperatures between 350 and 900°C , and Reaction 11 is slow but reaches a maximum at 600°C (16). Calkins's (5) observation of CS_2 formation at $T > 850^\circ\text{C}$ at the expense of H_2S indicates that Reactions 9 and 10 are possible. Our observation of the decrease in CS_2 and the increase in COS yields at 550°C as t_{res} decreases supports Reactions 10 and 11. This observation also agrees with our previous results for Green River shale which found greater yields of COS from vacuum pyrolysis than in a self-purging reactor (7). Some of the sulfur from pyrite decomposition may also be trapped in the organic matrix (17).

We didn't detect elemental sulfur (S_2 and S_8), nor did Boudou et al. (5) find elemental sulfur from isothermal pyrolysis of non-oxidized coal. In our study, the

parent/daughter pair of 64/32, which could either be SO₂ or S₂, had a very weak signal.

Because the evolution of sulfur gases always precedes that of hydrocarbon gases, organic sulfur components in coal, in general, seem to be more readily released during pyrolysis than non-heteroatom hydrocarbons. Lester et al. (18) made the same observation in their study with model compounds, although they found sulfur compounds and hydrocarbons evolve nearly simultaneously from coal in a chemical shock tube in which the coal residence time was 1.2-1.5 ms. We also find that T_{max} for H₂S and hydrocarbons both increase with the rank. The same trend is also seen for thiols and thiophenes. The increase in T_{max} for hydrocarbons with rank reflects coal becoming more carbonaceous with rank.

4. Conclusion

We studied the evolution of individual sulfur species during coal pyrolysis. Sulfur dioxide is the only sulfur gas that evolves at T < 200 °C, and all organic sulfur gases as well as COS, CS₂, and H₂S are found at 400-500°C, the temperature range of pyrolysis. The decomposition of pyrite at ~550°C produces H₂S, COS, and CS₂. Both gas-solid reactions and gas-phase secondary reactions are responsible for sulfur gas formation. The evolution of sulfur gases precedes that of hydrocarbon gases.

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Table 1. Parent/Daughter Mass Combination Employed in Sulfur Gas Identification.

Sulfur Species		Parent/Daughter Mass
H ₂ S	Hydrogen Sulfide	34/32 or 34
CH ₃ SH	Methanethiol	48/45 or 48
CO ₂	Carbonylsulfide	60/32
C ₂ H ₅ SH	Ethanethiol	62/29
(CH ₃) ₂ S	Dimethylsulfide	62/47
SO ₂	Sulfur Dioxide	64/48
CS ₂	Carbon Disulfide	76/32
C ₃ H ₇ SH	Propanethiol	76/42
C ₄ H ₄ S	Thiophene	84/45
CH ₃ C ₄ H ₄ S	Methylthiophene	97/53

Table 2. Elemental Analysis and Sulfur Forms (MAF basis) of Illinois No.6 Seam High Volatile Bituminous Coal (ILHVB) and Blind Canyon Seam High Volatile Bituminous Coal (BCHVB).

	ILHVB	BCHVB
% C	77.7	77.9
% H	5.7	6.0
% N	1.4	1.4
% O ^a	9.8	14.2
% Total S	5.4	0.5
Sulfur Forms:		
% Org. S	2.4	0.38 ^b
% Pyrite	3.0	N.A.
% Sulfate	0.01	N.A.

a. By difference.

b. Ref. 8.

Acknowledgments

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Table 3. Yields (STP cc/g coal) of Sulfur Gases under Different Pyrolysis Conditions.

Sweep Gas Flow Rate (cc/m):		34	34	169
Coal Sample Size (g):		0.52	2.54	2.58
Sulfur Species		Std. Run	High P _{vol}	Shorter t _{res}
H ₂ S	1st Peak	4.800	6.161	5.503
	2nd Peak	8.230	8.702	9.113
	Total	13.030	14.863	14.616
COS	1st Peak	0.057	0.071	0.067
	2nd Peak	0.110	0.138	0.254
	Total	0.167	0.209	0.321
CS ₂	1st Peak	0.017	0.019	0.002
	2nd Peak	0.087	0.040	0.036
	Total	0.104	0.059	0.038
CH ₃ SH		0.202	0.221	0.184
C ₂ H ₅ SH		0.031	0.036	0.029
(CH ₃) ₂ S		0.006	0.006	0.005
C ₃ H ₇ SH		0.007	0.009	no data
C ₄ H ₉ S		0.022	0.020	0.023
CH ₃ C ₄ H ₄ S		0.076	0.072	0.089

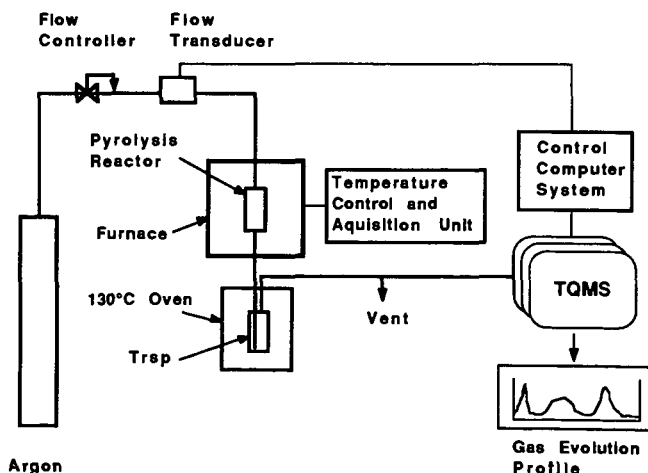


Fig. 1. Schematic of experimental set-up for gas evolution studies.

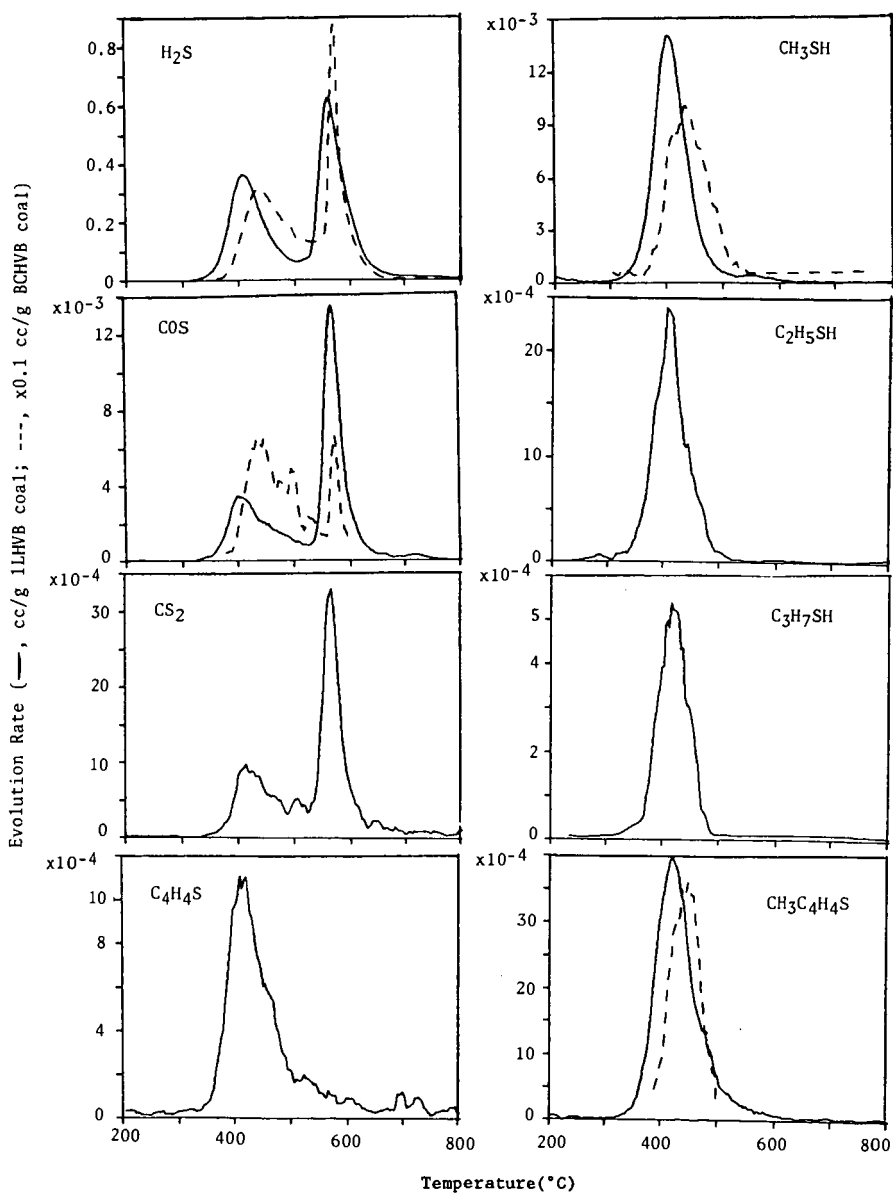


Fig. 2. Evolution profiles of eight sulfur gases.

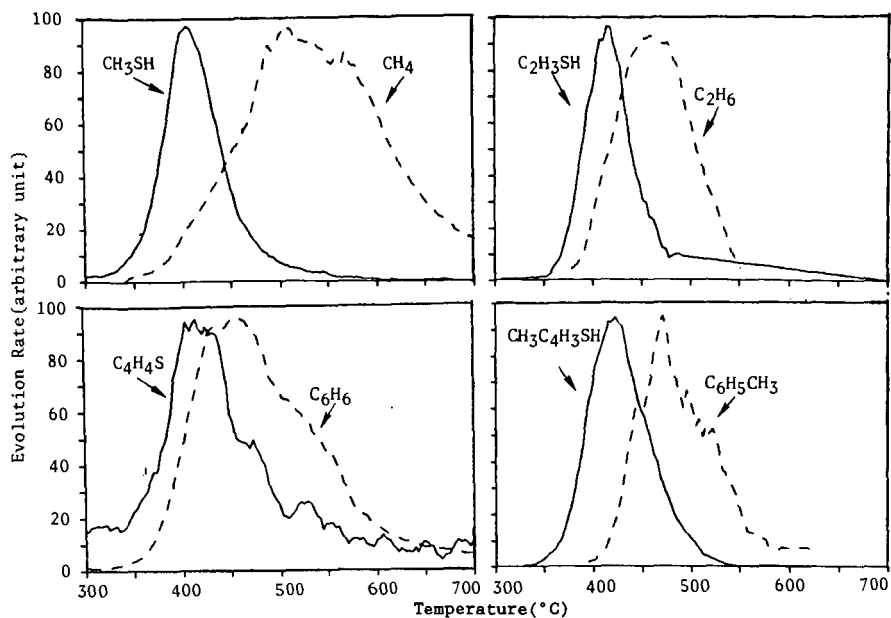


Fig. 3. Comparison of sulfur gas evolution with hydrocarbons.

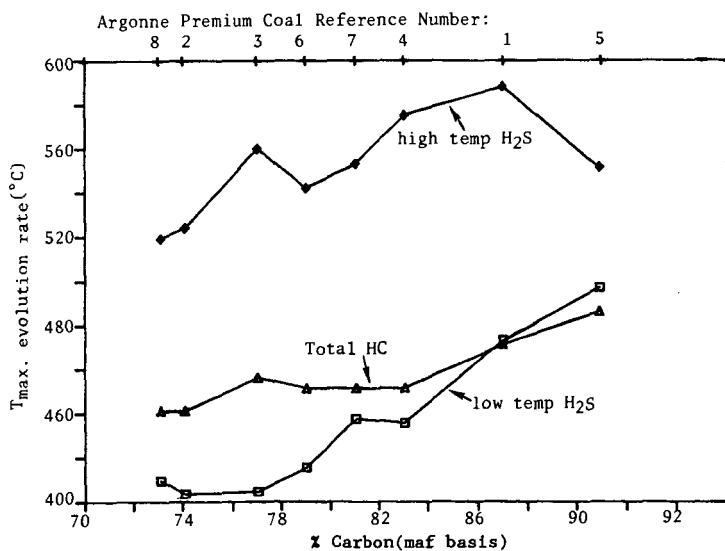


Fig. 4. Variation of T_{max} for H_2S and total hydrocarbon gases and naphtha (HC) with coal rank